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The Analysis of the Cosmic-Ray Absorption Curve

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A method of solving the integral equation of absorption

$$f(s)=\int_0^\infty \phi(\mu)\exp(-\mu s)d\mu$$

is developed which gives the function ϕ as a series of Laguerre orthogonal functions, whose coefficients are determined from the power series expansion of a function $F(x)$. This in turn is simply related to the given function $f(s)$; in case the latter is given numerically, the expansion may be accomplished by the method of least squares. The function ϕ (called the absorption coefficient spectrum of the radiation) is determined for cosmic rays at several altitudes and latitudes. In each case there are two maxima of intensity, one at $\mu=0.06$ and one at $\mu=0.6$ (meters water)$^{-1}$. The minimum of intensity occurs at $\mu=0.25$, or $1/\mu=4$ m water $=30$ cm mercury. This is also the range of the rays responsible for the inflection points of the Compton-Stephenson high altitude curve, but no consistent explanation of the correlation is found. The spectrum also shows a range of negative intensity, indicating the presence of secondary radiations. In no case is there any evidence for a line structure of the spectrum. No basis is found for restricting the assumption of exponential absorption to apply only to equatorial data; neither is any evidence discovered which makes the assumption a necessary one at any latitude. Only data on the absorption in air and water are considered; several points are indicated at which the existing data require extension.

I. INTRODUCTION

THE cosmic-ray absorption curve has been analyzed by Millikan and his co-workers,[1] by Kulenkampff,[2] Lenz[3] and others. These interpretations have been based on various assumptions, some of which are common to all, while others are specific with one writer. The most common assumption is that a unidirectional beam of homogeneous rays is absorbed according to an exponential law, which corresponds roughly to supposing that the rays are electromagnetic in nature. This second form of the assumption cannot be maintained unqualifiedly, since it is known, both from the existence of a latitude effect and from experiments with expansion chambers, that there are charged particles among the rays. However, the assumption of exponential absorption has had a certain measure of success and the results of different workers show a consistency which is remarkable in view of the serious objections advanced by L. D. Weld against the method of calculation.[4] This method consists in introducing the second assumption that the rays have a line spectrum and then guessing both the absorption coefficient and intensity of each line; from this guess a synthetic curve can be constructed and compared with the observed absorption curve. When a sufficiently close fit is obtained, the guess is supposed to be

[1] R. A. Millikan and G. H. Cameron, Phys. Rev. **37**, 240 (1931). I. Bowen, R. A. Millikan and V. H. Neher, Phys. Rev. **44**, 246 (1933).
[2] V. H. Kulenkampff, Phys. Zeits. **30**, 561 (1929).
[3] E. Lenz. Zeits. f. Physik **83**, 194 (1933).
[4] L. D. Weld, Phys. Rev. **40**, 713 (1932).

correct. This is, perhaps, not an entirely fair description of the procedure, since there are certain features of the observed curve which can be used as aids in determining the trial values of the coefficients,[3] but in its essentials it is correct. Weld devised a procedure for correcting the first trial values by the method of least squares[5] and found the corrections to be inadmissably large, from which he concluded that the results were meaningless.

Since it is probable that few writers have considered the assumption of a line spectrum as other than a simplification, it becomes desirable to eliminate it. This is one purpose of the present paper; a second is to apply the assumption of exponential absorption in a uniform manner to data of various types, which has not hitherto been possible because of the method of calculation.

II. Theory of Absorption Curves

Consider first a beam of unidirectional but inhomogeneous radiation, so that the intensity of that portion of the radiation whose absorption coefficient lies between μ and $\mu+d\mu$ is $\phi(\mu)d\mu$. The function $\phi(\mu)$ may be called the absorption coefficient spectrum of the radiation, or simply its spectrum if no confusion can result from the omission of the modifier. After passing through a thickness s of matter, the total intensity will be

$$f(s)=\int_0^\infty \phi(\mu)\exp(-\mu s)d\mu. \tag{1}$$

If, in addition to being inhomogeneous, the radiation is incident upon the surface $s=0$ from all directions with equal intensity, the total intensity at s will be ($\sigma=s/\cos\theta$)

$$I(s)=\int_0^{\pi/2} f(s/\cos\theta)\sin\theta d\theta = s\int_s^\infty [f(\sigma)/\sigma^2]d\sigma. \tag{2}$$

As Gross[6] has shown, this relation may be solved for f:

$$f=I-s(dI/ds)=I\{1-[d(\log I)/d(\log s)]\}. \tag{3}$$

The first form of Eq. (3) yields a simple graphical method of constructing the f-curve from the I-curve: at abscissa s draw the tangent to the I-curve, continuing it until it intersects the I-axis. The projection of this point on the ordinate at s will be a point on the f-curve. This graphical method becomes very inaccurate for large values of s, and the logarithmic form is preferrable for numerical calculation.

The function $I(s)$ may also be written

$$I(s)=\int_0^\infty \theta(\mu)\exp(-\mu s)d\mu; \tag{4}$$

substitution of Eq. (1) in the second form of Eq. (2) yields

$$\theta(\mu)=(1/\mu^2)\int_0^\mu \mu\phi(\mu)d\mu, \tag{5}$$

or

$$\phi=2\theta+\mu(d\theta/d\mu). \tag{6}$$

The problem presented by the cosmic-ray data is the determination of $\phi(\mu)$ from a knowledge of $I(s)$; two procedures are available: (1) f may be calculated from Eq. (3) and Eq. (1) then solved for ϕ; or (2) Eq. (4) may be solved for θ, and ϕ calculated from Eq. (6). Both methods involve the solution of an integral equation of the same form (Eqs. (1) and (4)); for reasons which will appear, the first procedure will be adopted, and $f(s)$ treated as a known function.

In Section VIII it will be important to be free of the assumption of uniform incidence from all directions; it will be noted that this assumption does not enter into Eq. (4), which is valid for any directional distribution whatever. It does enter, through Eq. (2), into Eqs. (5) and (6).

III. Solution of Eq. (1)

Eq. (1) arises in numerous physical problems, e.g., the determination of the "luminosity-depth" function of a thick x-ray target from the observed angular distribution of its radiation. If s is a complex number, the equation may also be made the basis of the theory of electric circuits.[7] In the particular cases that s is a pure imaginary or that f and ϕ are analytic functions, it may be solved by Fourier's theorem. Unfortunately, neither of these special cases is realized in the cosmic-ray problem. Carson[7] has based a treatment of

[5] An alternative method to Weld's is K. Pearson's *Method of False Position*, Phil. Mag. **5**, 658 (1903).

[6] B. Gross, Zeits. f. Physik **83**, 214 (1933).

[7] J. R. Carson, *Electric Circuit Theory and the Operational Calculus*, McGraw-Hill (1926). Eq. (29), p. 21 is identical with Eq. (1) above, except for notation.

TABLE I. *Values of the Laguerre functions* $u_n(\alpha)$.

α	u_0	u_1	u_2	u_3	u_4	u_5	u_6	u_7
0.0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
.1	0.95123	0.85611	0.76574	0.67997	0.59864	0.52161	0.44872	0.37984
.2	.90484	.72387	.56100	.41502	.28478	.16920	.06725	− .02207
.3	.86071	.60250	.38302	.19839	.04505	− .08033	− .18080	− .25916
.4	.81873	.49124	.22924	.02402	− .13231	− .24678	− .32572	− .37478
.5	.77880	.38940	.09735	− .11357	− .25757	− .34701	− .39263	− .40368
.6	.74082	.29633	− .01482	− .21928	− .33974	− .39534	− .40213	− .37349
.7	.70469	.21141	− .10923	− .29750	− .38664	− .40382	− .37103	− .30581
.8	.67032	.13406	− .18769	− .35214	− .40505	− .38257	− .31283	− .21730
.9	.63763	.06376	− .25186	− .38672	− .40085	− .34000	− .23830	− .12048
1.0	.60653	.00000	− .30327	− .40435	− .37908	− .28305	− .15584	− .02455
1.1	.57695	− .05770	− .34329	− .40781	− .34405	− .21736	− .07193	.06403
1.2	.54881	− .10976	− .37319	− .39953	− .29943	− .14749	.00863	.14097
1.3	.52205	− .15661	− .39414	− .38170	− .24832	− .07705	.08237	.20372
1.4	.49659	− .19863	− .40720	− .35622	− .19330	− .00885	.14693	.25107
1.5	.47237	− .23618	− .41332	− .32475	− .13654	.05499	.20085	.28283
1.7	.42741	− .29919	− .40818	− .24954	− .02450	.16386	.27440	.30251
2.0	.36788	− .36788	− .36788	− .12263	.12263	.26978	.30248	.24409
2.2	.33287	− .39945	− .32621	− .03817	.19886	.30098	.27572	.16742
2.5	.28650	− .42976	− .25069	.07760	.27531	.29583	.18967	.03093
2.7	.25924	− .44071	− .19573	.14375	.30132	.26467	.11502	− .05761
3.0	.22313	− .44626	− .11157	.22313	.30680	.18966	− .00279	− .16655
3.5	.17377	− .43443	.02172	.30048	.24663	.03091	− .16689	− .25299
4.0	.13534	− .40601	.13534	.31578	.13534	− .11729	− .24962	− .22040
4.5	.10540	− .36890	.22397	.28326	.00906	− .21846	− .24421	− .10929
5.0	.08209	− .32834	.28730	.21889	− .10603	− .25994	− .17158	.02671
5.5	.06393	− .28768	.32763	.13718	− .19428	− .24574	− .06336	.14275
6.0	.04979	− .24894	.34851	.04979	− .24894	− .18919	.04979	.21195
7.0	.03020	− .18118	.34727	− .11072	− .26045	− .01560	.20664	.19050
8.0	.01832	− .12821	.31137	− .22589	− .17705	.14530	.22019	.03274
9.0	.01111	− .08887	.26106	− .28883	− .05138	.23107	.11984	− .12958
10.0	.00674	− .06064	.20888	− .30770	.07412	.23134	− .02321	− .20823
11.0	.00409	− .04087	.16143	− .29561	.17454	.16667	− .14545	− .18442
12.0	.00248	− .02727	.12146	− .26523	.24044	.06792	− .21169	− .08846
13.0	.00150	− .01804	.08945	− .22652	.27269	− .03693	− .21493	.03166
14.0	.00091	− .01185	.06474	− .18633	.27752	− .12845	− .16704	.13397
15.0	.00055	− .00774	.04618	− .14878	.26292	− .19648	− .08811	.19359
17.0	.00020	− .00326	.02269	− .08858	.20443	− .25622	.17127	.12175
20.0	.00005	− .00086	.00731	− .03597	.11143	− .21636	.23169	− .04623
25.0	.00000	− .00009	.00098	− .00649	.02845	− .08586	.17664	− .22921
30.0	.00000	− .00001	.00012	− .00099	.00561	− .02276	.06740	− .14417

Heaviside's operational methods on the equation, practically without restriction on the complex nature of s, so that Heaviside's solutions are available. However, they are at best convergent power series and at worst asymptotic series; in either case they are valuable only for restricted ranges of μ and s. The following solution is valid for wider ranges of the variables, and has not previously appeared in the literature, to the writer's knowledge.

It is convenient to introduce the dimensionless variables

$$\xi = s/s_0, \qquad \alpha = 2s_0\mu, \tag{7}$$

where s_0 is any convenient unit of length. Eq. (1) then becomes

$$f(\xi) = (1/2)\int_0^\infty \Phi(\alpha)\exp(-\alpha\xi/2)d\alpha, \tag{8}$$

where

$$\Phi(\alpha) = \phi(\mu)/s_0. \tag{9}$$

This function may be expanded as a series of Laguerre orthogonal functions:[8]

$$\begin{aligned}\Phi(\alpha) &= \Sigma a_n u_n(\alpha),\\ u_n(\alpha) &= (1/n!)\exp(-\alpha/2)L_n(\alpha),\end{aligned} \tag{10}$$

where L_n is the nth Laguerre polynomial. On substituting Eq. (10) into Eq. (8), the latter becomes

$$f(\xi) = \Sigma a_n(\xi-1)^n(\xi+1)^{-n-1}, \tag{11}$$

since it is readily shown that (cf. Sommerfeld, reference 8, page 94)

$$(1/2n!)\int_0^\infty L_n(\alpha)\exp[-\alpha(\xi+1)/2]d\alpha = (\xi-1)^n(\xi+1)^{-n-1}. \tag{12}$$

[8] Courant-Hilbert, *Methoden der Mathematischen Physik*, 1st Ed., p. 79; A. Sommerfeld, *Ergänzungsband*, p. 75.

On introducing the abbreviations

$$x=(\xi-1)/(\xi+1), \quad F(x)=(\xi+1)f(\xi), \quad (13)$$

Eq. (11) becomes

$$F(x)=\Sigma a_n x^n. \quad (14)$$

Thus, in order to obtain the coefficients of Eq. (10), it is merely necessary to calculate $F(x)$ from $f(s)$ and then approximate it by a polynomial. This may be done by the method of least squares, or any other available procedure. To plot the function $\Phi(\alpha)$, the numerical values of the Laguerre functions are required; these are given in Table I[9] for $n=0\cdots7$.

IV. The "Electrometer Zero" and the "Low Absorption Limit"

The data obtained from the ionization chamber measurements of Millikan and Cameron[1] and of Regener[10] are the values of $I(s)$+const., the constant being the "electrometer zero." This is not determined directly, but is obtained by extrapolation on the assumption that $I(s)\to a \exp(-\mu_0 s)$ for large values of s, or alternatively, that $I(s)\to aG(\mu_0 s)$ (G being the Gold function). Both of these procedures are based on the idea that there is a "low absorption limit" to the cosmic-ray spectrum analogous to the short wave limit of an x-ray spectrum. This idea is an obvious one if the cosmic rays are electromagnetic radiation, but its verification would be remarkable if this assumption is not correct. It is important to clarify the issues on this point before proceeding further, since they are also related to Weld's results.

If the idea of a low absorption limit is to be adopted, it leads naturally to replacing Eq. (4) by

$$I(s)=\int_{\mu_0}^{\infty}\theta(\mu)\exp(-\mu s)d\mu, \quad (4.1)$$

μ_0 being the smallest value of μ for which $\theta(\mu)$ is not identically zero. If this integral be subjected to repeated partial integration, it results in

$$I(s)=\exp(-\mu_0 s)\{\theta(\mu_0)/s + \theta'(\mu_0)/s^2+O(1/s^3)\}, \quad (4.2)$$

θ' being the derivative of θ. If it be assumed that θ approaches zero in a continuous manner as μ approaches μ_0 from above, $\theta(\mu_0)$ vanishes and $I\to\theta'(\mu_0)[\exp(-\mu_0 s)]/s^2$. An examination of Regener's data from this point of view leads only to the conclusion that $\theta'(\mu_0)$ is very large, but does not yield any value for μ_0. The data would have to be extended to enormously greater depths before they could be used to determine the low absorption limit on this basis. Alternatively, one may suppose that $\theta(\mu_0)$ is not equal to zero which is equivalent to supposing that $I\to aG(\mu_0 s)$; on this basis it is possible to obtain values of all three quantities, μ_0, $\theta(\mu_0)$ and the electrometer zero, but μ_0 is only slightly greater than its estimated probable error—the data would even tolerate a small negative value. This is one of Weld's results, in essence.

Under these circumstances, the only reasonable tentative assumption to make is that μ_0 and $\theta(\mu_0)$ are both zero, which will be done in the following. This point can be satisfactorily cleared up only by a direct determination of the electrometer zero, which will increase the accuracy of the μ_0 calculation. This assumption leads to a value of 0.73 v/hr for the zero of Regener's instrument, as compared to the value 0.78 diffidently adopted by him. If the zero of the Millikan-Cameron instrument be determined so that their data agree with Regener's, a value of 0.95 ion/cm³/sec. is obtained, as compared to the value 1.2±0.2 adopted by them.

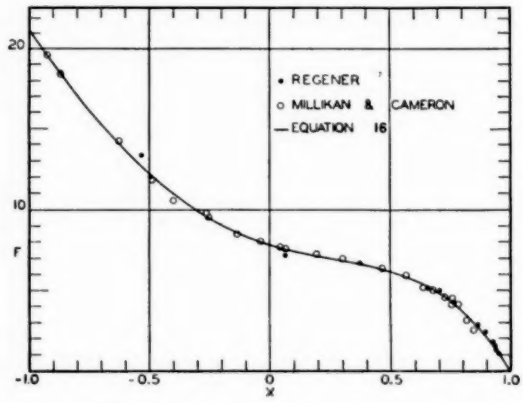

FIG. 1. Graph of $F(x)$, numerical data as in Eq. (15).

[9] Table I was prepared by Mrs. G. S. Monk, to whom the author is also indebted for carrying out other parts of the calculations, particularly those involving least squares methods.

[10] E. Regener, Phys. Zeits. **34**, 308 (1933); Zeits. f. Physik **74**, 433 (1932).

V. The Analysis of the Combined Data of Regener and Millikan and Cameron[10a]

When combined as just described, the data of Regener and Millikan and Cameron furnish a set of values of $I(s)$ in the range $8.25<s<240$ equivalent meters of water. From these a large graph of $\log I$ *vs.* $\log s$ was constructed; its slope was calculated numerically and the value of $f(s)$ obtained from Eq. (3). It was found preferable to use the observed rather than the interpolated values of I in Eq. (3), since the latter were subject to systematic errors of the same order as the random errors of the former; the systematic errors of the derivative could not be avoided.

If the method of solution outlined in Section II were applied to these data, the resulting function $\phi(\mu)$ would be very uncertain because of the lack of data over the range $0<s<8.25$. Fortunately, the simple device of replacing s by $s-8$ and ϕ by $\phi \exp(-8\mu)$ leaves the equation for $f(s)$ unaltered and eliminates the necessity of extrapolation. This is Heaviside's operation of *shifting;* the new function obviously represents the spectrum of the radiation at the new origin of s. The second of the two methods outlined at the end of Section II would not lend itself as readily to this modification.

It is also necessary to choose the value of s_0 (Eq. (7)). This quantity is found to determine the degree of the polynomial needed to approximate $F(x)$, but the dependence is not critical. In this case, it was found satisfactory to take $s_0=6$; the value 4 or 8 would have increased the degree considerably, but 5 or 7 would presumably have been about as satisfactory as 6. If h is the equivalent depth below the top of the atmosphere, the foregoing leads to the numerical relations

$$s=h-8, \quad \xi=s/6, \quad \alpha=12\mu,$$
$$x=(h-14)/(h-2). \quad (15)$$

[10a] The new data of Kramer, Zeits. f. Physik **85**, 411 (1933) were unfortunately inaccessible at the time these calculations were made. They differ by more than the experimental error from those of Millikan and Cameron. If they had been used in the present section, some quantitative differences would have resulted, and the difficulties to be mentioned in the next section would have been accentuated. The data of Corlin, Nature **133**, 63 (1934) seem to bear out the tentative conclusion of Section IV above.

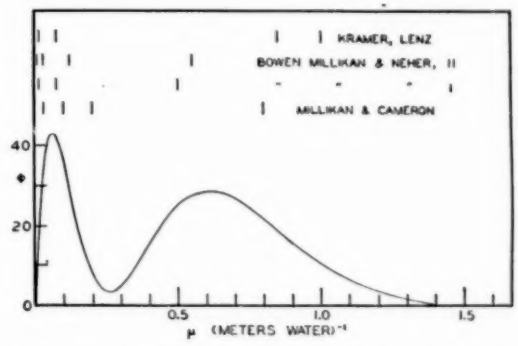

FIG. 2. Absorption coefficient spectrum of the cosmic rays at barometric pressure 8 m water = 59 cm mercury.

In Fig. 1, the points represent the values of $F(x)$ calculated as described and the curve is the graph of the polynomial

$$F(x)=7.90-4.40x+6.17x^2-6.20x^3-3.47x^4 \quad (16)$$

(units: ions/cm³ at 1 atmos.). The coefficients of this polynomial were obtained by drawing a smooth curve through the points and interpolating the values of F for $x=0, \pm\frac{1}{2}, \pm 1$. The Lagrange interpolation formula[11] was then used to find the polynomial of fourth degree defined by these five points.

From the coefficients of the polynomial, the function $\phi(\mu)$ can be calculated immediately from Eqs. (9) and (10); its graph is shown in Fig. 2. This is seen to have two well-defined but broad maxima at $\mu=0.06$ and 0.62 (meters water)$^{-1}$. For comparison, the line spectra assumed by various authors are indicated at the top of the figure.[12] To assist the reader in evaluating this comparison it should be remarked (1) that the present method has sufficient resolving power to have separated peaks at $\mu=0.5$ and 0.8 had the data required it; (2) that the numbers of disposable constants used in the present calculation and by Bowen, Millikan and Neher in their Table I synthesis are equal; (3) that the last-mentioned synthesis represents the data quite as accurately as the curve of Fig. 1, but no more so. The author believes that the comparison is unfavorable to the idea that the spectrum consists of lines.

[11] Courant-Hilbert, reference 8, 1st Ed., p. 83.

[12] In the case of Lenz's analysis only the absorption coefficients of the primary radiation are indicated. The data are taken from references 1 and 3.

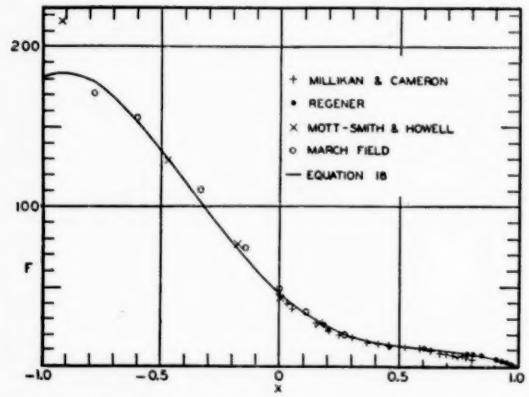

FIG. 3. Graph of $F(x)$, numerical data as in Eq. (17).

VI. THE SPECTRUM AT HIGHER ALTITUDE

The spectrum of the cosmic rays at a point 4 equiv. meters below the top of the atmosphere may be obtained by combining the ionization data obtained by Mott-Smith and Howell[13] and Bowen, Millikan and Neher[1] with the underwater data discussed in the last section. The validity of this combination depends on assumptions regarding phenomena occurring at the air-water interface which have not yet been tested in sufficient detail, but which may be tentatively accepted. In this way values of $I(s)$ are obtained for the range $4<h<240$, but the data for the smaller values of h are by no means as reliable as those for larger. Choosing $s=h-4$, and $s_0=4$, so that

$$\xi=(h-4)/4, \quad \alpha=8\mu, \quad x=(h-8)/h, \quad (17)$$

it was found that

$$F(x)=47.4-131.4x+128.5x^2 +25.4x^3-85.8x^4+15.9x^5. \quad (18)$$

The coefficients of this polynomial were obtained in a slightly different way from those of Eq. (16): by graphical interpolation values of F were obtained for $x=0, \pm0.2, \pm0.4, \cdots \pm1.0$. These values were then weighted proportionally to $1/(1-x)$ to take account of the preponderant amount of the data for large values of s, and the polynomial determined by least squares. No doubt it would have been better statistical practice to have omitted the interpolation and treated the original data; a glance at Fig. 3 also suggests that a polynomial of the sixth degree might have fitted the data more closely. It is not clear, however, that these technical improvements would have increased the significance of the results (see Section VII).

The solid curve of Fig. 4 represents ϕ as determined from the coefficients of Eq. (18). The two peaks have scarcely shifted their positions, but their relative and absolute heights have altered because of the smaller amount of filtering at the higher altitude. The broken curve represents ϕ as calculated from Fig. 2 by multiplying its ordinates by exp $(+4\mu)$; the two curves should be identical, but actually the agreement is only qualitative. It is possible that the difference is due entirely to inaccuracies of the data and the calculations, but if real it must be ascribed to phenomena occurring at the air-water interface.

VII. THE INFLUENCE OF SECONDARY RADIATIONS

The negative values of ϕ which are very pronounced in Fig. 4 require discussion. They may be considered as due to secondary radiations, which were not considered in the developments of Section II. There, ϕ was supposed to be the intensity of the primary radiation, and therefore essentially positive. If the influence of secondaries be taken into account, this restriction is removed, but the interpretation of ϕ becomes less simple.

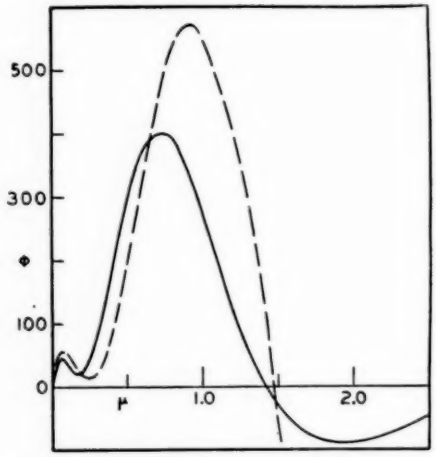

FIG. 4. Absorption coefficient spectrum of the cosmic rays at barometric pressure 4 m water = 30 cm mercury.

[13] L. Mott-Smith and L. G. Howell, Phys. Rev. **42**, 314 (1932).

The problem of the secondary radiations accompanying the primary cosmic rays is a complex one and no complete discussion of it is possible at this time. The following sketch omits many essentials, but will serve to bring out a point which has not received sufficient consideration. Let $\phi_1(\mu)$ be a function which can be given the interpretation which has previously been assigned to $\phi(\mu)$, and suppose that primary radiation of absorption coefficient μ produces secondary radiation of absorption coefficient $\mu_2 > \mu$. For simplicity, tertiary, etc., radiations will be neglected. Suppose also that the secondaries travel in the same direction as the primaries; then it may be shown that[14] the ionization produced by the complex beam is given by

$$f(s) = \int \phi_1(\mu)\{a(\mu) \exp(-\mu s) - b(\mu) \exp(-\mu_2 s)\} d\mu, \quad (19)$$

where a and b are essentially positive functions. To perform the integration, μ_2 must be known as a function of μ, or preferably μ as a function of μ_2, say $\mu = g(\mu_2)$. Then the change of variable from μ to μ_2 in the second term of the integral reduces Eq. (19) to the form of Eq. (1) with

$$\phi(\mu) = a(\mu)\phi_1(\mu) - b[g(\mu)]\phi_1[g(\mu)]g'(\mu). \quad (20)$$

This new function ϕ is not restricted to positive values, and the negative ordinates of Fig. 4 are explicable.

However, it is the function ϕ_1 which is of interest for the problem of the origin and nature of the cosmic rays, and having found ϕ, the problem of determining ϕ_1 is encountered. It is by no means certain that this problem possesses a unique solution, even granting that the functions a, b and g, were known from theory, which they are not. Furthermore, Eq. (20) was derived on highly simplified assumptions; the true equation will be much more complex. It seems that no reliable conclusions concerning this point can be reached by analytical means: the problem is essentially an experimental one. Methods must be devised for measuring the primary rays alone, without admixture of secondary effects.[15] Unless the experimental data are such that the simple interpretation of Section II is valid, the function ϕ obtained by the procedure outlined there has little more significance than the original unreduced data $I(s)$.

VIII. The Latitude Effect

R. A. Millikan[16] has recently advanced an hypothesis to account for the latitude effect, according to which the cosmic rays at accessible altitudes in equatorial regions are entirely composed of photons (or neutrons) while the rays reaching the earth at higher latitudes are contaminated with electrically charged particles. Bowen, Millikan and Neher have interpreted this hypothesis to mean that only absorption data obtained in equatorial regions may be analyzed on the assumption of exponential absorption. It is therefore necessary to analyze data from the two regions in a uniform manner in order to determine whether there is an experimental basis for this distinction.

In view of the asymmetry of the directional effect in equatorial regions[17] it is not justifiable to assume that the rays are incident from all directions with uniform intensity. (This assumption is implicit in the use of Gold functions.) This point alone makes the hypothesis difficult to defend, for an explanation of the asymmetry of the directional effect apparently requires magnetic deviability of the rays. Supposing that this objection can be answered, there still remains the question, is there any experimental basis for applying the assumption of exponential absorption only to equatorial data? Such a basis is not apparent from the $I(s)$ curves;[18] the ϕ-curves cannot be given the same meaning for the two regions; there remains only the possibility that the θ-curves (cf. Eq. (4)) which do not depend on the assumption of all-sided incidence, will reveal the difference to be expected on this hypothesis.

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[14] See Kulenkampff, reference 2, and T. H. Johnson, Phys. Rev. **41**, 545 (1932). This point has also been emphasized by Millikan.

[15] For a more detailed discussion of this problem, see A. H. Compton and R. J. Stephenson, Phys. Rev. **45**, 441 (1934).

[16] R. A. Millikan, Phys. Rev. **43**, 666 (1933). Also Bowen, Millikan and Neher, reference 1.

[17] B. Rossi, Phys. Rev. **45**, 212 (1934). T. H. Johnson, Phys. Rev. **43**, 834 (1933); **44**, 856 (1933). L. Alvarez, Phys. Rev. **43**, 835 (1933).

[18] A. H. Compton and R. J. Stephenson, reference 15.

To obtain material for such a comparison, the data given in Table I, "observed" column, of the paper by Bowen, Millikan and Neher[1] were taken as representing the equatorial data. (The electrometer zero was altered in such a way as to increase each value by 0.0081 unit.) The ratio of the ionization at March Field to that in Panama and Peru was next determined from Fig. 3 of the same paper; thus two $I(s)$ curves were available, one for equatorial and one for northern latitudes. The calculations for the coefficients of θ (shifted to 4 m water below the top of the atmosphere) were then carried out uniformly (and simultaneously) with those already described in Section VI.

The resulting functions θ and their difference are plotted in Fig. 5. It is believed from various

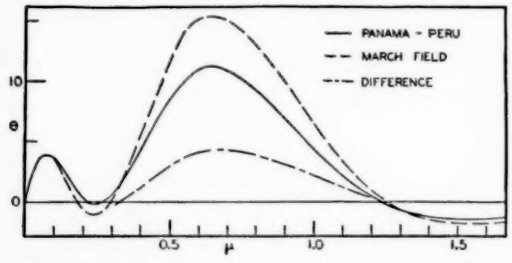

FIG. 5. Comparison of $\theta(\mu)$ at two different latitudes. From data of Bowen, Millikan and Neher, reference 1.

indications interpreted in the light of previous experience that both θ-curves are too low in the range $\mu<0.3$, and both too high in the region $0.3<\mu<1.0$. Their relative height in the latter range should not be much affected by these errors. The only experimental basis for maintaining that the Panama-Peru curve is significant, while the March Field curve is meaningless, would be a complete lack of correlation between the difference curve and that for Panama-Peru. In fact a complete and obvious correlation exists.[19] Hence, either both curves are meaningless, or both significant, so far as these data can be considered as reliable.

IX. Discussion

In evaluating the results obtained, it is important to understand that the successful calculation of ϕ has no theoretical significance whatever. Within limits, almost any function $f(s)$ can be represented by an integral of the type of Eq. (1), and these limits are greatly extended by the presence of secondary effects in the measurements, by experimental error, and by the impossibility of making measurements at infinite depths. Hence the justification of the assumption of exponential absorption cannot be found in the success of these calculations. Even if the cosmic rays consisted entirely of r-particles (i.e., particles having a definite range and ionizing their paths uniformly)[15] a ϕ-curve could still be deduced from the I-curve, provided only that the latter exhibited no discontinuities of slope. This condition would imply a continuous distribution of ranges. In this case, however, it would not be possible to make a unique assignment of a given value of μ to a single type of ray.[20]

The results obtained on the latitude effect cannot easily be understood on the assumption of exponential absorption. They seem to require two kinds of rays for a given value of μ, one of which is magnetically deflectable and the other not. Since it is quite easy to see that r-particles of two different ranges may contribute to the value of ϕ for a single value of μ, the artificiality of this assumption disappears when the rays are assumed to be r-particles. Neither theory affords a satisfactory explanation of the approximate proportionality of the difference between the two curves of Fig. 5 to the ordinates of either; however, this quantitative result is not to be given much weight, nor is it to be expected that either theory will be valid in the simple form discussed here.

It would seem that on any theory of the nature of the rays, the existence of the two maxima in Fig. 2 could be taken as evidence of two more or less distinct components. It should be noted, however, that there is considerable latitude in the

[19] It seems probable that an entirely similar result would have been obtained if ϕ-curves had been constructed. This is perhaps not surprising since it is also probable that the directional effect will show an asymmetry at any latitude provided the measurements are made at a sufficiently high altitude. The assumption of uniform incidence from all directions would then not be justified anywhere.

[20] If the number of r-particles having a range between r and $r+dr$ is given by $\mu\exp(-\mu r)dr$, then it is easily shown that $f(s)=\exp(-\mu s)$. On the r-particle basis, the ϕ-curve therefore represents the analysis of the rays into elementary distributions of this form. It is obvious that rays of every range contribute to the value of ϕ for a given value of μ.

possible descriptions of the two components. On the basis of exponential absorption, two extreme possibilities present themselves according as it is assumed that Fig. 2 is or is not appreciably affected by the presence of secondary rays not yet in equilibrium with their primaries. In the former case, the curve represents (qualitatively at least) the spectrum of the primary rays, and the two components are presumably of distinct extra-terrestrial origin. In the latter case, the primary rays may have a spectrum of only one maximum, and the minimum may be due entirely to the negative contribution of secondaries (cf. Section VII) whose origin is terrestrial. The second possibility is extreme and may perhaps be dismissed because the experiments on transition effects do not suggest the existence of secondaries of such penetrating power.

It is none the less interesting to note that these secondaries would have a mean range of about 4 m water = 30 cm mercury, which is about the range of the rays responsible for the two inflection points of the Compton-Stephenson high altitude *f*-curve. So far as existing data are concerned, this quantitative agreement must be ascribed to chance, for it is not possible to obtain a consistent explanation of the result on either the assumption of exponential absorption or on that of *r*-particles. On the former basis, the two inflection points of the *f*-curve would require that the ordinates of Fig. 2 be very definitely negative at $\mu=0.25$; the data might tolerate a value $\phi=-5$ at this point, but it is doubtful if this would be sufficient. On the other hand, if the inflection points are due to *r*-particles of 30–40 cm range,[18] these could not possibly affect Fig. 2, which was constructed entirely from data obtained at pressures greater than 60 cm. It is desirable that further data on this point be obtained.

Perhaps the most definite conclusion to be derived from this study may be formulated as a warning against too simple an interpretation of the cosmic-ray absorption curve. It is certainly influenced by many different effects and its analysis will require further carefully planned experimental work.

It is a pleasure to acknowledge many stimulating conversations on these matters with Professor A. H. Compton, and to mention again the assistance of Mrs. G. S. Monk, without which the work would have lagged interminably.

The Band Spectrum of CS

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The emission spectrum of CS has been photographed under high dispersion (0.28A per mm) permitting a considerable extension of the data of the main $A^1\Pi \rightarrow x^1\Sigma$ system ($\nu_e = 38{,}912.15$ cm^{-1}), and revealing a new system $C^1\Sigma \rightarrow B^1\Sigma$ ($\nu_0(0,0) \leqq 39{,}905.1$ cm^{-1}). The anomalies of bands with extra heads or displaced origins (noted by Jevons) have been examined in detail and found to be due to rotational perturbations more widespread and striking than any previously reported.

INTRODUCTION

A BAND spectrum discovered in 1911 by Fowler and Strutt[1] was investigated by Martin[2] and attributed by him to CS. A vibrational analysis of the spectrum made by Jevons[3] in 1927 failed to account for several strong bands, and revealed striking irregularities in the positions of the origins of bands in several progressions. Also, irregular values for the head-origin separations of many bands were found, and certain bands seemed to possess two R heads, rather than the single one expected from a $^1\Pi \rightarrow {}^1\Sigma$ or a $^1\Sigma \rightarrow {}^1\Pi$ transition.

It seemed desirable, therefore, to photograph the spectrum under much higher dispersion in order to obtain an explanation of the above phenomena. A rotational analysis would, in addition, enable one to compare the CS molecule with its important homologue CO, and with the equivalent molecules SiO and PN.

It is felt that a rather full account of these observations is justified, since the high dispersion used has (1) revealed band structures of hitherto unreported forms, (2) permitted explanation of these anomalous structures in terms of peculiarly vigorous and widespread rotational perturbations, (3) lead to the discovery and rotational analysis of a second system ($C^1\Sigma \rightarrow B^1\Sigma$) of CS bands, and (4) made possible a more complete vibrational and a partial rotational analysis of the main system ($A^1\Pi \rightarrow x^1\Sigma$).

[1] Fowler and Strutt, Proc. Roy. Soc. **A86**, 111 (1911).
[2] L. C. Martin, Proc. Roy. Soc. **A89**, 127 (1913).
[3] W. Jevons, Proc. Roy. Soc. **A117**, 351 (1928).

EXPERIMENTAL PROCEDURE

Excitation of the spectrum

Although the spectrum of CS may be obtained in a sulfur-carbon arc, or an arc employing carbon poles saturated with CS_2, the most satisfactory source appears to be a discharge tube (with very narrow flattened capillary) into which CS_2 is admitted. It was found that a pressure of about 0.1 mm and a very low rate of CS_2 inflow resulted in a spectrum of great intensity and comparative purity. A higher pressure decreased the intensity, and made "air bands" predominant; it also hastened the fogging of the window and shortened the life of the tube. For the virtual elimination of sulfur bands,[4] as well as the air bands, from low-dispersion spectrograms, special precautions were required. Not only was a new tube and a very low pressure necessary, but it was found essential to keep the column of excited gas as cool and free of sulfur as possible by stopping the discharge for a moment after every second of exposure. Such intermittent operation probably allowed the sulfur to deposit on the glass walls, with the consequent almost complete absence of the more troublesome S_2 bands. After a tube had been used for several hours, it was found to emit more strongly and to require almost no CS_2 inflow. This is perhaps explained by an accumulation of

[4] Martin's plates, which were used by both Jevons and Martin, show strong sulfur bands extending to wave-lengths as short as $\lambda 2820$, thus concealing much valuable information. Grating plates, concerned only with intense bands and hence shorter wave-lengths, were unaffected by sulfur bands and therefore taken with continuous operation.

polymerized CS[5] molecules capable of vaporizing and maintaining the discharge.

Photographing the spectrum

A large number of spectrograms were made with various pressures, voltages, and types of plates. Four quartz spectrographs and three gratings were used. The majority of the data used in the vibrational analyses were obtained from spectrograms made with a Hilger E 315 quartz spectrograph giving a dispersion ranging from 7A per mm at λ2400 to 18A per mm at λ3200. The rotational analyses were based on photographs taken in the second and third orders of the 21-ft. grating of this laboratory and the 34-ft. grating of the Massachusetts Institute of Technology, which, in the third orders, give dispersions of 0.66 and 0.28A per mm, respectively. Eight to twenty-four hour exposures were normally required, though the most important bands were photographed with an anastigmatic system which greatly reduced this time. Thus by placing a cylindrical lens just in front of the plate, in a manner described by Oldenberg,[6] the intensity was increased to such an extent that exposure times of from 10 to 30 minutes sufficed for third order plates, even when an unusually narrow slit was used.

Measurements

An iron comparison spectrum obtained from an International Astronomical Union Arc[7] was employed throughout.[8] The wave-length separations of the sharper lines of a single band should be accurate to within 0.005A, or 0.08 cm^{-1}. The work involved in making rotational analyses was much lightened by employing enlargements; and so fine is the structure of these bands (the R branch of the (0,1) band has an apparent extent of only 1A) that a dispersion of 1A per 50 mm in the enlargements was found to be none too much. Records made on a photographic densitometer were used in estimating the intensities of the bands, and of the lines within single bands.

[5] Cf. Dewar and Jones, Proc. Roy. Soc. **A83**, 527 (1910); **A85**, 574 (1911).
[6] Oldenberg, J. O. S. A. **22**, 441 (1932).
[7] Trans. Internat. Astron. Union **3**, 84 (1928).
[8] Wave-lengths were taken from Jackson's tables, Proc. Roy. Soc. **A130**, 404 (1931).

General Description of the Spectrum

The spectrum of CS consists of at least two systems composed of bands which are degraded to the red and lie between λ3300 and λ2400. The main or first system, which arises from a $^1\Pi \rightarrow {}^1\Sigma$ transition, contains 65 bands. A second weaker system, representing a $^1\Sigma \rightarrow {}^1\Sigma$ transition not involving the $^1\Sigma$ state of the main system, includes 4 bands sufficiently intense and unobscured by overlapping of the main system for photography at high dispersion.

The Main System: $A^1\Pi \rightarrow x^1\Sigma$

Vibrational Analysis

The partial elimination of sulfur bands has revealed a large number of hitherto unobserved CS bands of longer wave-length, and use of contrast plates and long exposures has brought out a few new heads on the short wave-length end of the spectrum. Thus the number of bands which have now been arranged in a two-dimensional array of the usual kind has been more than doubled. Most of the data for heads and origins were obtained from two plates made on different quartz spectrographs and with different sources. More precise values for the wave numbers of origins and heads of about twenty of the strongest bands were obtained from grating plates. Thus the accuracy of the wave numbers of the origins varies from about 0.1 cm^{-1} to 4 cm^{-1}. In every case, the position of the origin was considered to be identical with that of the first Q line, or "Q head." (The calculated distances, for the (0,1) band, of the $Q(1)$ and $Q(2)$ lines from the true origin are 0.10 cm^{-1}, and 0.31 cm^{-1}, respectively.)

The bands of this system are all degraded to the red. They have, with a few exceptions, single P, Q, R branches, and form sequences which overlap considerably. The arrangement of the new bands in the vibrational array follows essentially the scheme of Jevons. As noted by him, the analysis is complicated by three anomalies: (a) certain bands appear to have two R heads; (b) the origins and heads of certain bands are displaced considerably from the expected positions (this was formerly attributed to vibrational perturbations); (c) in some bands no origins or heads are apparent.

TABLE I. *Bands of the main system* ($^1\Pi \rightarrow {}^1\Sigma$).

v', v''	Head	Int.	ν_{vac},cm^{-1}	$\nu_h - \nu_0$	v', v''	Head	Int.	ν_{vac},cm^{-1}	$\nu_h - \nu_0$	v', v''	Head	Int.	ν_{vac},cm^{-1}	$\nu_h - \nu_0$
8,4	*R*	0	41639.13		4,4	*R*	1	37881.2	10.0	7,9	*Q*		34753.2	
4,1	*R*	0	41618.4		4,4	*Q*		37871.2		2,5	*R'*	2	34676.5	27.6
5,2	*R*	0	41336.2	10.2	0,1	*R'*	20	37543.95	18.86	2,5	*R*		34666.0	17.1
5,2	*Q*		41326.0		0,1	*R*		37538.74	13.65	2,5	*Q*		34648.9	
9,5	*R*	0	41305.4	4.8	0,1	*Q*		37525.09		8,10	*R*	2	34512.4	12.4
9,5	*Q*		41300.6		1,2	*R'*	15	37339.*n*	38.	8,10	*Q*		34500.0	
6,3	*R*	1	41038.5	6.3	1,2	*R*		37309.53	8.2	3,6	*R*	2	34477.2	19.0
6,3	*Q*		41032.2		1,2	*Q**		37301.34		3,6	*Q*		34458.2	
10,6	*R*?	0	40973.2		2,3	*R*	11	37117.94	14.00	4,7	*R*	3	34260.8	13.2
2,0	*R*	1	40892.3	9.3	2,3	*Q*		37103.94		4,7	*Q*		34247.6	
2,0	*Q*		40883.0		3,4	*R*	8	36902.42	14.80	5,8	*R*	2	34058.2	17.2
7,4	*R*	1	40732.2	5.8	3,4	*Q*		36887.62		5,8	*Q*		34041.0	
7,4	*Q*		40726.4		4,5	*R*	6	36662.68	9.94	6,9	*R*	2	33834.7	12.1
3,1	*R*	3	40637.3	12.3	4,5	*Q*		36652.74		6,9	*Q*		33822.6	
3,1	*Q*		40625.0*n*		5,6	*R*	4	36433.09	13.5	7,10	*R*	1	33609.4	12.4
8,5	*R*	3	40417.5		5,6	*Q*		36419.62		7,10	*Q*		33597.0	
4,2	*R*	4	40361.05	7.66	0,2	*R'*	8	36287.65	21.75	8,11	*R*	3	33370.6	13.7
4,2	*Q*		40353.39		0,2	*R*		36280.65	14.75	8,11	*Q*		33356.9	
9,6	*R*	1	40096.3		0,2	*Q*		36265.90		3,7	*Q*?	0	33262.4	
5,3	*R*	5	40091.41	8.41	6,7	*R*	2	36181.6	10.5	9,12	*R*	1	33127.0	9.3
5,3	*Q*		40083.0		6,7	*Q*		36171.1		9,12	*Q*		33117.7	
1,0	*R**	7	39837.0		1,3	*R'*	7	36102.	46.	4,8	*R*	0	33077.8	12.0
2,1	*R*	11	39620.97	11.77	1,3	*R*		36063.45	7.8	4,8	*Q*		33065.8	
2,1	*Q*		39609.20		1,3	*Q**		36055.68		5,9	*R*	0	32890.9	18.5
7,5	*R*	4	39511.5	7.5	7,8	*R*	0	35927.7	10.6	5,9	*Q*		32872.4	
7,5	*Q*		39504.0		7,8	*Q*		35917.1		6,10	*R*	0	32679.0	14.8
3,2	*R*	10	39378.94	11.80	2,4	*R'*	6	35893.6	23.2	6,10	*Q*		32664.2	
3,2	*Q*		39367.15		2,4	*R*		35885.97	15.60	7,11	*R*	0	32465.9	14.3
4,3	*R*	9	39115.20	8.04	2,4	*Q*		35870.38		7,11	*Q*		32451.6	
4,3	*Q*		39107.16		3,5	*R*	5	35684.22	17.5	8,12	*R*	2	32240.3	16.5
9,7	*R*	2	38904.5	8.7	3,5	*Q*		35666.74		8,12	*Q*		32223.8	
9,7	*Q*		38895.8		4,6	*R*	5	35454.6	14.6	9,13	*R*	0	32006.6	15.8
5,4	*R*	7	38858.93	9.50	4,6	*Q*		35440.0		9,13	*Q*		31990.8	
5,4	*Q*		38849.43		5,7	*R*	4	35240.3	13.3	10,14	*R*	0	31766.6	6.5
0,0	*R'*	20	38814.22	17.21	5,7	*Q*		35227.0		10,14	*Q*		31760.1	
0,0	*R*		38809.74	12.73	0,3	*R'*	3	35044.8	25.8	11,15	*R*	0	31517.4	8.5
0,0	*Q*		38797.01		0,3	*R*		35035.1	16.1	11,15	*Q*		31508.9	
1,1	*R*	20	38568.20	7.7	0,3	*Q*		35019.0		8,13	*R*	0	31123.6	17.4
1,1	*Q**		38560.51		6,8	*R*	3	35002.4	11.4	8,13	*Q*		31106.2	
2,2	*R*	12	38363.07	13.00	6,8	*Q*		34991.0		9,14	*R*	0	30902.8	15.6
2,2	*Q*		38350.07		1,4	*R'*?	1	34875.	56.	9,14	*Q*		30887.2	
3,3	*R*	5	38134.00	13.06	1,4	*R*		34827.8	8.4	11,16	*R*	0	30441.0	7.9
3,3	*Q*		38120.94		1,4	*Q**		34819.4		11,16	*Q*		30433.1	
8,7	*R*	1	38017.3		7,9	*R*	1	34763.6	10.4					

n = nebulous; ? = identification uncertain. For convenience, the wave-lengths of the 6 strongest bands are appended to Table IV.

* Jevons (cf. reference 3) mistook the *R'* and *R* heads in the $v' = 1$ progression for the *R* and *Q* heads, respectively, thereby obtaining too small values for the origin displacements.

In Table I are included wave numbers of all measured band origins and *R* heads of this main $^1\Pi \rightarrow {}^1\Sigma$ system. When two apparent *R* heads occur, both are tabulated, the inner and outer being designated as *R* and *R'*, respectively. Vibrational quantum numbers and head-origin intervals are listed, as well as intensities estimated from densitometer records. The general appearance of the spectrum under low dispersion may be seen from Fig. 1.

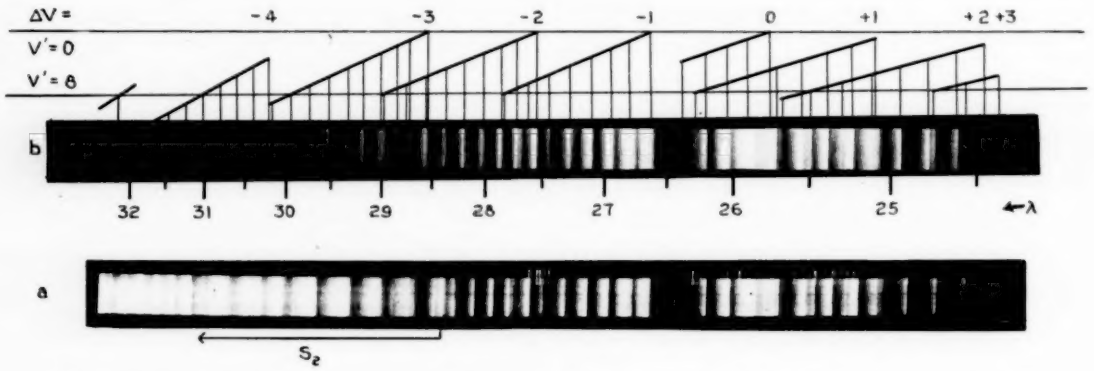

FIG. 1. (1a) contains many sulfur bands obscuring a large number of CS bands. (1b) is virtually free of all impurities. The scale is slightly greater in the lower enlargement.

TABLE II. *Main System. Vibrational energy differences.*

V	$\Delta G'(v'+\frac{1}{2})$	$\Delta G''(v''+\frac{1}{2})$
0	1035.43 cm^{-1}	1272.10 cm^{-1}
1	1048.73	1259.16
2	1017.12	1246.17
3	986.00	1233.44
4	976.6	1220.9
5	949.5	1208.3
6	929.0	1195.0
7	904.	1182.0
8	885.	1168.5
9	871.	1157.0
10	839.	1144.0
11		1131.
12		1118.
13		1104.
14		1090.
15		1076.

The accuracy, which varies considerably, is indicated by the number of decimal places included.

Weighted averages of the first vibrational-energy differences, $\Delta G(v+\frac{1}{2})$, are contained in Table II. Here it is important to note that for the lower ($x^1\Sigma$) state these first differences are perfectly regular, within the limits of experimental error. In the case of the first differences for the ($^1\Pi$) state, however, marked irregularities occur at low v' values. The extent, amounts, and cause of these will be discussed in connection with the rotational structure. The following formula represents the smoothed frequencies of the band origins:

$$\nu_0(v', v'') = 38{,}912.15 + [1072.3(v'+\tfrac{1}{2}) - 10.3(v'+\tfrac{1}{2})^2] - [1285.1(v''+\tfrac{1}{2}) - 6.5(v''+\tfrac{1}{2})^2]. \quad (1)$$

Since the second differences $\Delta^2 G(v)$ are virtually constant over the range of the data obtained, it was felt that the addition of terms in higher powers of v' and v'' would be without significance. From the above equation, which is not applicable to bands of perturbed progressions, we derive the constants included in Table III.

The intensities, shown in Table IV, vary essentially in the manner to be expected from the Franck-Condon theory, except for the unusually high intensity of the $v'=8$ progression. The lower limb of the narrow parabola describing the intensity maxima is attenuated, since the weak bands composing this limb are obscured by strong overlapping bands of other sequences.

TABLE III. *Vibrational constants of the main system.*

	$A^1\Pi$	$x^1\Sigma$
ω_e	1072.3 cm^{-1}	1285.1 cm^{-1}
x_e	0.00961	0.00506
D_e	27,373. cm^{-1}	62,841. cm^{-1}
	3.377 volts	7.752 volts
ν_e	38,912.15 cm^{-1}	
	4.800 volts.	

TABLE IV. *Intensities of the main system bands.*

Wave-lengths of the origins of the most intense bands are: (2,1) λ2523.91; (0,0) λ2576.75; (1,1) λ2592.55; (2,2) λ2606.78; (0,1) λ2664.093; (2,3) λ2694.33.

v'\v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	20	20	8	3													
1	7	20	15	7	1												
2	1	11	12	11	6	2											
3		3	10	5	8	5	2	0									
4		0	4	9	1	6	5	3	0								
5			0	5	7		4	4	2	0							
6				1	*	*		2	3	2	0						
7					1	4			0	1	1	0					
8					0	3	5	1			2	3	2	0			
9						0	1	2					1	0	0		
10							0	0							0		
11																0	0

* Hidden by more intense bands.

The dissociation energy values, calculated by linear extrapolation, must be regarded essentially as upper limits for the actual dissociation energies. Since ν_e+D' exceeds D'' by only about 5 percent, this suggests strongly that the dissociation products for the two states are really the same.

Anomalies

All bands whose origins are given closely by Eq. (1) and whose branches appear virtually regular invariably possess single P, Q and R branches,[9] and their head-origin intervals, ($\nu_h - \nu_0$), vary in the normal way with v' and v''.

On examination of all bands observed at high dispersion, however, it is found that practically every band exhibits some anomalies, such as: double R-branch heads, displaced origins, distinct fringes beyond otherwise normal heads, abnormal ($\nu_h - \nu_0$) values, and irregular branches.

In endeavoring to explain the existence of so many irregular features in a presumed $^1\Pi \rightarrow {}^1\Sigma$ system, several possibilities were considered.

[9] For example: the progressions $v'=3,5$.

Thus the appearance might be affected by the superposition of another system of CS or some other molecule (perhaps[10] CS_2), or the assignment of the bands to a $^1\Pi \rightarrow {}^1\Sigma$ system might be incorrect. In a given band the presence of a fringe near the R head might result from $\Delta J = +2$ transitions or accidental groups of impurity lines.[11] No one of these hypotheses proved to be capable of accounting in an unforced manner for more than a few of these anomalies. However, the postulate of a perturbing state having closely the same energy and ω as the $^1\Pi$ state and interacting strongly with it has been found capable of explaining all the observed facts. Since the moment of inertia of CS is so large and hence the rotational levels so closely spaced, a strong perturbation would be expected to affect a range of J-values *larger* than that observed in lighter molecules, with the production of branches of hitherto unobserved form. The precise appearance of a given band will depend upon a number of factors whose variation can explain in a natural manner the wide variety of anomalies mentioned above and now to be discussed in some detail.

(1) Double-headed bands

(*a*) *Observations.* The R and R' heads exhibited by a number of the CS bands are most striking in the case of the (0,1) and (0,2) bands. These are of high intensity and are practically free from the superposition of other bands. Although their P and Q branches appear essentially single, neither the $(\nu_{R'} - \nu_0)$ nor the $(\nu_R - \nu_0)$ interval is consistent with the regular bands. Under highest dispersion, these R and R' heads present curious features. (Fig. 2.) The inner, or R head ceases to resemble a normal head, and seems rather to be merely a series of lines coming to an abrupt convergence. The intensity is great near this convergence point, and if the branch continues back upon itself from here, it does so with greatly diminished intensity. The outer, or R' head presents an even more anomalous aspect. It consists of an unresolved block fringed on the *short*-wave-length side with lines of irregular intensity and position, and on the *long* wave-length side with a regular series of faint lines. The structure of the R' heads in the (0,1) and (0,2) bands is somewhat different, showing that the appearance of the "double-head" varies with v'', although its existence depends on a perturbation in the *upper* state only.

(*b*) *Interpretation.* That this anomaly is to be ascribed to a widespread rotational perturbation of the *upper* state alone is conclusively demonstrated by examining the bands of the striking $v' = 2$ progression, which shows the whole range of phenomena under discussion. Of these bands, those for which $v'' = 0$ and 1 appear regular; each possesses a single R head which is separated by the expected amount from the origin. The bands for which $v'' = 2$ and 3 also appear essentially regular, but formless fringes of lines just beyond the R head are *always* present. In the band $v'' = 4$, however, this fringe has drawn together into a sort of blurred head; and, finally, in the $v'' = 5$ band we have a sharp line-like R' head quite like that of Fig. 2.

If we consider the $^1\Pi$ state to be perturbed by another electronic level, a typical diagram of such a perturbation is shown in Fig. 3. Here there is a depression of the levels for J slightly less than J_p,—the J-value at which the unperturbed energy curves would cross; and the levels for J slightly greater than J_p are raised.[12]

Now the appearance of a given band originating in the perturbed $^1\Pi$ state will depend not only upon J_p but also upon the J-value at which the head would normally be formed,—say J_h, as may be seen from the corresponding Fortrat diagrams. Here, as is shown in Fig. 4, each branch is composed of two fragments somewhat concealed by overlapping in the Q and P branches, but very obvious in the R branch. The R branch fragment for the low J's will converge to an apparent head, the high-J fragment tending to form a head-like structure of greater or less sharpness, according to the exact

[10] This possibility is ruled out because the gross structure of the system requires for each of the electronic states involved a *single* vibrational frequency whose value is quite different from those reported by Dennison and Wright (Phys. Rev. **38**, 2077 (1931)), for CS_2.

[11] It seems exceedingly unlikely that such transitions should produce branches of the strength and form observed, and independent of the various discharge conditions used. Since nearly half of the bands show these fringes, they can hardly be attributed to impurities.

[12] For a general theoretical discussion of rotational perturbations see Kronig, Zeits. f. Physik **50**, 347 (1928) and Ittmann, Zeits. f. Physik **71**, 616 (1931).

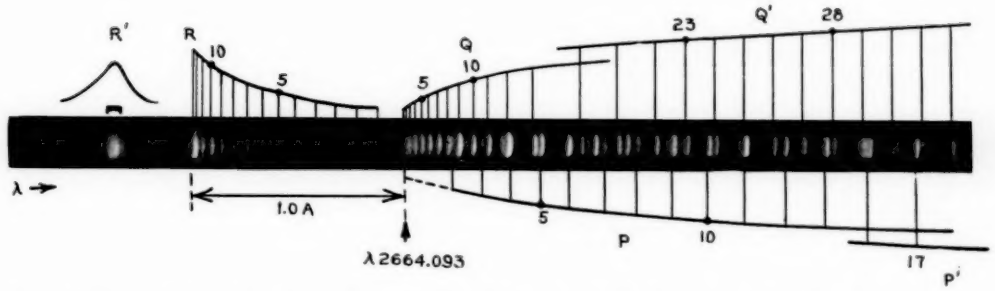

FIG. 2. The (0,1) band of the main system of CS, under high dispersion, showing the anomalous appearance of the R and R' heads discussed in the text.

relationship between J_p and J_h. This R' head will be sharpest for J_p slightly less than J_h.

For any one v'' progression, we are dealing with the same v', and hence the same J_p. But as we pass along such a progression, B'', and therefore $(B''-B')$, will decrease proportionally more rapidly than $(B''+B')$. But these quantities determine J_h and $(\nu_h-\nu_0)$. Thus[13]

$$J_h=-1-[(B'+B'')/2(B'-B'')];$$

$$\nu_h-\nu_0=-(B'+B'')^2/4(B'-B'')$$

and therefore we expect both J_h and $(\nu_h-\nu_0)$ to increase with v''. In the case of perturbed bands in which $J_p<J_h$, this means that we should expect the three intervals $(\nu_R-\nu_0)$, $(\nu_{R'}-\nu_0)$, $(\nu_{R'}-\nu_R)$ likewise to increase with v''. The outer or R' head should at the same time become continually sharper and approach the position of the "unperturbed" head. This progressive variation is illustrated in Fig. 4.

TABLE V. *Anomalous heads of the main system progression* $v'=2$.

Band	ν_0 cm^{-1}	ν_R cm^{-1}	$\nu_{R'}$ cm^{-1}	$\nu_R-\nu_0$	$\nu_{R'}-\nu_0$
2,0	40883.0	40892.3	none	9.3	—
2,1	39609.20	39620.97	none	11.77	—
2,2	38350.07	38363.07	faint	13.00	—
2,3	37103.94	37117.94	broad	14.00	—
2,4	35870.38	35885.97	35893.6	15.60	23.2
2,5	34648.9	34666.0	34676.5	17.1	27.6

In Table V, which gives the data on these intervals for the $v'=2$ progression, it is to be noted that as v'' increases and the R' head grows from a formless fringe to a very sharp head, the various intervals *increase* regularly.

[13] See, for example, Jevons' *Report on Band-Spectra of Diatomic Molecules*, p. 44.

Double-headed bands of other progressions likewise behave in this characteristic fashion. In the P and Q branches, overlapping of the fragments is predicted, which is in complete accord with the observations.

(2) Origin perturbations

The Q heads of the bands of the progressions $v'=1$ and $v'=4$ are displaced towards the red from their expected positions by about 18 cm^{-1} and 6 cm^{-1}, respectively. Jevons, who first noted this anomaly, originally attributed it to a "vibrational" perturbation (a phenomenon no longer recognized) of the v' levels concerned. These bands we now regard as a special case of extra-headed bands in which the rotational perturbation reaches a maximum at a very low value of J. If $J_p=6$, for example, besides a large displace-

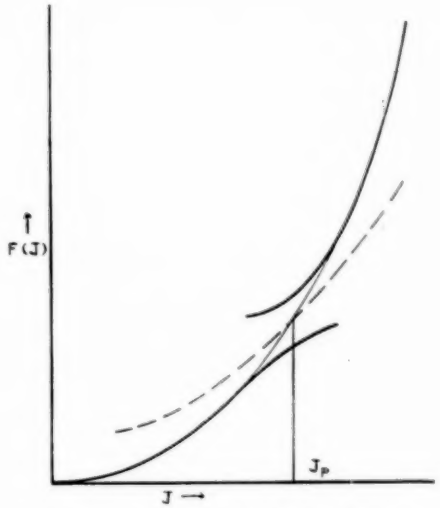

FIG. 3. An upper state perturbation (schematic). For simplicity, we have suppressed the distinction between c and d levels, and included but one of the several perturbing sub-states (dotted).

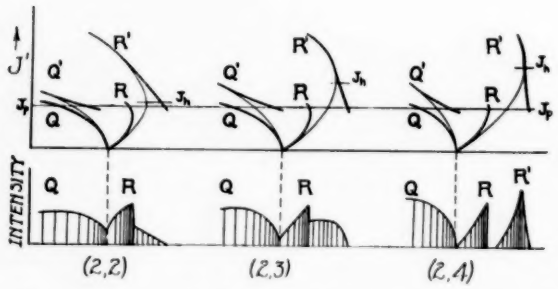

FIG. 4. Schematic Fortrat and intensity diagram for three bands of the striking progression $v'=2$ ($J_p \leqq 17$), showing the dependence of the exact form of the band structure on v''. P branches are suppressed for simplicity, and "unperturbed" branches are drawn in lightly in the upper diagram. In the lower diagram, for the sake of clarity, only a fraction of the lines actually observed are indicated. Note that as v'' increases from 2 to 4 both J_h and the head-origin intervals increase, and the outlying fringe draws together to form a sharp "head."

ment of the lines for which J is very close to 6, there will be a smaller but appreciable displacement of the very first lines. Thus the Q head as a whole, and hence the apparent origin, is shifted. In the (1, 2) band, for example, the R branch forms a very abrupt R head at about the 6th line, and a break in the Q branch occurs for about the same J. A faint and blurred R' head is found about 30 cm^{-1} beyond the R head, and there is evidence of a second Q fragment overlapping the first. The P branch is untraceable.

TABLE VI. *Band heads of the $v'=1$ progression, their intervals and displacements* from normal positions.*

Band	$\nu_R-\nu_0$	$\nu_{R'}-\nu_0$	ν_0 $-\nu_0$ norm.	ν_R $-\nu_R$ norm.	$\nu_{R'}$ $-\nu_R$ norm.
1,1	7.7 cm	—	−18. cm	−25. cm	—
1,2	8.2 cm	38. cm	−18. cm	−27. cm	+3. cm
1,3	7.8 cm	46. cm	−18. cm	−29. cm	+9. cm
1,4	8.4 cm	56. cm	−18. cm	−31. cm	+4. cm

* (−) displacements are towards smaller wave numbers.

Thus the situation would be described completely by Figs. 3 and 4 if we there decreased J_p appropriately. It should be noted that the inner or R head will be displaced more than the origin, and if the outer R branch forms a head,—the R' head, it should be at or *beyond* the position of the normal head. For the three bands of the progression $v'=1$ where a measurable R' head is found, all the above requirements are satisfied. (See Table VI.)

(3) Other anomalous features

Rotational perturbations will immediately account for other irregular features, such as: bands with no apparent Q or R heads, suddenly terminated branches, and overlapping branch fragments. Furthermore, in a few cases confusion does result from the superposition of bands of other CS systems, and above λ3300 the CS spectrum is concealed almost completely by the ever-present main system of S_2.

Rotational Analysis

(1) Difficulties

It is unfortunate from the standpoint of obtaining accurate rotational constants that the strongest bands contain the most pronounced perturbations, and that no one of the 25 bands photographed under high dispersion is perfectly normal. Even in the most regular bands, such as those for which $v'=5$, a complete rotational analysis is out of the question; for: (a) the first two or three Q lines are scarcely resolved, at best; (b) the R lines are nearly symmetrical in intensity about J_h, and always only partially resolved[14]; (c) many lines of the P branch (the weakest branch in the band) are obscured by the intense and closely spaced Q lines; (d) the presence of so many perturbations lessens the value of the usual intensity and "second difference" relationships of such great use in line-assignments in regular bands. Thus, for example, the Λ-doubling in the upper $^1\Pi$ state renders the relationship: $R(J)-Q(J) \leqq Q(J+1)-P(J+1)$ useful only for unperturbed lines of low J, and it permits the perturbations in the Q branch and in the R, P branches to occur at quite different values of J'.

(2) Actual procedure

(*a*) *Fairly complete analyses.* Analyses of the (0,1) and (0,2) bands were carried through far enough to permit the evaluation of the most essential constants and to verify rather conclusively our explanation of the extra R heads. In each of these bands, definite values of J'' were assigned to the first 13 lines in the three branches. It was found that for $J \leq 9$, the approx-

[14] In the (5,6) band, $J_h \leqq 18$, which means that about 36R lines are included in the head-origin interval of 0.9A.

imate relation $R(J)-Q(J)\cong Q(J+1)-P(J+1)$ held, but that for larger J, rapidly mounting "defects" appeared. In attempting to avoid this situation, all other likely systems of line interpretations and numberings were considered, but with no success. The correctness of the original scheme is shown by several considerations: it satisfies the combination principle, and requires regular and almost constant second differences, $\Delta^2F(J)$, for both states. [These second differences are not to be confused with the ordinary double differences, $\Delta_2F(J)$.] But the most satisfying result is the close agreement of the two sets of data for the upper level common to the two bands.

Table VII includes the vacuum wave numbers for those lines of the above two bands which have been arranged into branch fragments. Table VIIb is a continuation of VIIa but with an altered assignment of the branch fragments. In neither case is there any appreciable "quantum defect" found for lines for which $J\leq 9$, and for these lines the resulting rotational energy terms may be described with the accuracy permitted by the data by simple expressions of the form: $F(J)=B(J^2+J)$, where $B'(0)$, $B''(1)$, and $B''(2)$ have the values 0.7595 cm^{-1}, 0.8115 cm^{-1}, and 0.8060 cm^{-1}, respectively.

The P and R lines' spacings remain regular in both bands up to $J\cong 14$, at which point displacements to the red set in. In the Q branches, however, similar displacements first appear at the lower J value: $J\cong 11$. This means, of course, that the $^1\Pi$ state c levels are affected by the perturbing state for J about 3 units less than is the case for the d levels. It is to be regretted that insufficient resolution prevents detailed following of the several branches and their associated displacements, since this would fix more closely the extent of the overlapping of the segments of any one branch,—with respect to both energy and J.

Attempts were made to continue the analyses of the (0,1) and (0,2) bands for the high-J parts of the branches (to be designated as the P', Q', R' fragments) which appeared on the spectrograms to be unperturbed. Although the Q' and P' fragments were easily identified and measured, the R' fragment consisted essentially of the broad but unresolved R' head fringed on either side by lines which could not be arranged in any convincing series.[15] We proceeded, therefore, by assuming that all R' lines were located at the center of this R' head, and by seeking that pair of numbering systems of the Q' and P' fragments for which the approximate relation $R(J)-Q(J)\cong Q(J+1)-P(J+1)$ gave the smallest and most well-behaved "quantum defect." The differences between successive energy terms could now be derived and compared with those obtained by extrapolation from the corresponding, known, low-J term differences, with the result that fairly accurate, absolute J-values

TABLE VII. *The main system bands (0,1), (0,2).*

(0,1) λ2664.093				(0,2) λ2756.615		
$P(J)$ cm^{-1}	$Q(J)$ cm^{-1}	$R(J)$ cm^{-1}	J	$P(J)$ cm^{-1}	$Q(J)$ cm^{-1}	$R(J)$ cm^{-1}
		37526.52*r*	0			36267.50
	37524.93*r*	27.97	1			68.93
37521.70*r*	24.74*r*	29.37	2	36262.54*r*	36265.74*r*	70.33
19.89	24.53*r*	30.69	3	60.91*r*	65.50*r*	71.71
18.05*s*	24.20	31.90	4	58.96	65.28	72.97
16.00*s*	23.76	33.04	5	57.12*r*	64.88	74.14
14.12*s*	23.25	34.08	6	55.21	64.46	75.31
11.96	22.69	35.07	7	53.12	63.94	76.35
09.77	22.05*s*	35.94	8	51.09	63.41	77.34
07.50	21.30	36.74	9	48.92	62.76*r*	78.20
05.16	20.42	37.46*r*	10	46.66	61.99	79.02
02.73*s*	19.40	38.00	11	44.33*s*	61.09	79.62*r*
00.17	18.20*r*	38.44*r*	12	41.93	60.02	80.19*r*
37497.51	16.44	38.60*r*	13	39.43*r*	58.49	80.56*r*
94.65*r*			14	36.77		80.65*r*
			15			
$P'(J)$ cm^{-1}	$Q'(J)$ cm^{-1}	$R'(J)$ cm^{-1}	J	$P'(J)$ cm^{-1}	$Q'(J)$ cm^{-1}	$R'(J)$ cm^{-1}
37494.65*r*			16	36236.77		
91.63			17	33.87		
88.12*r*			18	30.56		
84.60			19	27.52*r*		
80.84	37513.38		20	24.12	36257.00	
77.40	10.97		21	20.96	54.66	
74.02	08.55		22	17.84	52.42	
70.72	06.55		23	14.73	50.68	
67.38	04.68		24	11.73	49.09	
64.01	02.78		25	08.67	47.52	
60.61	00.90		26	05.57	45.98	
57.16	37498.98		27	02.46	44.34*s*	
53.66	96.91		28	36199.23	42.60	
50.03	94.94		29	96.00	40.93	
46.36	92.80	center of	30	92.74	39.21	
42.68	90.65	unresolved	31	89.42	37.30	center of
38.95	88.25	"head" at	32	86.05	35.46	unresolved
35.04	86.03	37544.00	33	82.61	33.64	"head" at
31.14	83.70		34	78.97	31.59	36287.29
27.15	81.18		35	75.56	29.52	
23.03	78.58		36	71.88	27.44*r*	
18.83	75.95		37		25.16	
14.47	73.12		38		22.77	
09.98			39		20.44	
05.34			40		17.81*r*	
00.37			41			
37394.91			42			
87.98			43			

r = resolution incomplete; *s* = superposition of another line. The J assignments for the P', Q', and R' lines form a consistent but not unique set.

[15] About ten lines of varying intensities and separations could be distinguished on each side of the R' head proper. It is significant that the longer-wave-length fringe, which is presumed to be composed of lines for which J considerably exceeds J_{p_1} possesses a much more nearly regular appearance than does the shorter-wave-length fringe, composed presumably of the most violently perturbed lines.

could be assigned the Q' and P' lines. This procedure gave quite consistent results in the two bands, and close agreement was found between their required upper state differences $[F_c'(J+1)-F_d'(J)]$.

In view of the considerable uncertainty introduced by the assumption that all the R' lines have the identical position on the spectrogram, these results cannot be expected to be unique. They do, however, afford strong evidence for the extra R heads' being related to the Q' and P' fragments in the manner required by our explanation, and also make possible a more significant estimate of the number of J-values for which two lines appear in each branch. In the most overexposed (0,1) spectrograms, this overlapping extends over perhaps 5 or 10 J-values, while the maximum separation of two lines of identical J is between 15 and 30 cm^{-1}. As mentioned below, these wave-number separations, although large, are entirely consistent with those found in the perturbed (0,0) band of the CO Angstrom system.[16]

An additional perturbation is found in the P' branch of the (0,1) band. As we pass up this branch from $P'(39)$, we find the lines displaced towards the red by rapidly increasing amounts, while the line $P'(43)$, at which the observed shift is greatest, is displaced about 6 cm^{-1} from its normal position. In the more intense (0,0) band, there are found similar displacements not only of the corresponding P' lines, but also of the Q' lines.

(*b*) *Partial analyses.* In many bands the Q or R branches,—rarely both, could be followed readily for fairly low J. Since in every case both the absolute and relative numberings of the Q and R lines were unknown, we were able to find for these bands only fairly accurate values of $(B'-B'')$ and rather inaccurate values of $(B'+B'')$. The results imply that $B'(v')$ (unperturbed) and $B''(v'')$ vary according to the relations:

$$B'(v')=B'(0)-\alpha'v'=0.7860-0.010(v'),$$

$$B''(v'')=B''(0)-\alpha''v''=0.8165-0.005(v'').$$

Close similarity of the α's is also required by the essential constancy of the head-origin interval within any one sequence. These equations show that

$$B_e'=0.7910\ cm^{-1}, \qquad B_e''=0.8190\ cm^{-1},$$

$$r_e'=1.56A, \qquad r_e''=1.53A.$$

It cannot be emphasized too strongly that on account of the presence in all bands of violent rotational perturbations, the line series, and hence the initial state energy levels responsible, do *not* conform to the theory applicable to normal bands. Thus there do not exist for the initial state strictly defined quantities B, D, α, etc., and precise values for them, if presented, would be of little physical significance.

Descriptions of the strongest bands, as well as estimated J-values at which the perturbations are central, are listed in terms of the upper vibrational state in Table VIII.

TABLE VIII. *Main system anomalies.*

v'	J_p	Origin displacement*	Number of R heads
0	15		2
1	6	−18 cm	2
2	17		1 ($v''\leq 2$)
			2 ($v''\geq 3$)
3	27		1
4	9	− 6 cm	2 (predicted)
5	28		1

*(−) displacements are towards smaller wave numbers.

The Electronic Transition

Since the most regular bands possess single P, Q and R branches, it is evident that the transition involves a $^1\Pi$ and a $^1\Sigma$ state. The *vibrational* analysis shows that it is the *upper* state which is perturbed, and the *rotational* analysis proves this upper state to be $^1\Pi$. For the presence there of both c and d levels is required in order to account for definitely different perturbations in the Q branch and the R, P branches for the *same* J'. This conclusion is in agreement with R and P branch intensity considerations, the almost certain presence of the $R(0)$ lines, the sign of the Λ-doubling, and the similar upper level classifications of the corresponding systems in the homologous molecules CO (4th positive,—cf. reference 16), PN,[17] and SiO.[18]

[16] Cf. Rosenthal and Jenkins, Proc. Nat. Acad. Sci. **15**, 896 (1929). Birge, Phys. Rev. **28**, 1157 (1926).

[17] Ghosh and Datta, Zeits. f. Physik **87**, 500 (1934).

[18] Saper, Phys. Rev. **42**, 498 (1932).

It is instructive to compare this main system of CS with the 4th positive system of CO: thus these two systems occur under similar excitation conditions, and the bands are alike in structure and intensity distribution. CO possesses larger constants ν_e, ω_e, B_e, and D_v'', as is in accordance with its smaller reduced mass; and the two CO states concerned have, presumably, the same dissociation products, as is probably the case for CS also. There is, furthermore, in this $^1\Pi$ state of CO a perturbation believed due to an interacting $^3\Pi$ state, and in our main system of CS we must assume the existence of a multiplet perturbing state, presumably $^3\Pi$ also.[19]

Since high vibrational levels of this interacting state may well be concerned in the perturbations, the strongest bands of a presumably weak intercombination system, $^3\Pi \rightarrow x^1\Sigma$, would lie in longer wave-length regions obscured on our plates by sulfur bands and, therefore, be unobservable.

The Second System of CS ($C^1\Sigma \rightarrow B^1\Sigma$)

Vibrational Analysis

Four of the strongest bands not included in the main system vibrational array and constituting one progression of what we shall call the second system of CS have been photographed under high and low dispersion. The bands have single P and R branches, and, therefore, arise from a $^1\Sigma \rightarrow {}^1\Sigma$ transition. They are degraded to the red, and possess faint R heads for which $J_h \leqq 4$.

Rotational analyses show these bands to have one level in common,—probably the initial level. The wave-lengths of the heads, and the assumed vibrational quantum numbers concerned, are as follows: The (0,0), (0,1), (0,2), and (0,3) R heads lie at λλ2505.19, 2587.327, 2674.465, and 2766.98, with relative estimated intensities of 2, 10, 5, and 1, respectively. This gives $\nu_0(0,0) \leqq 39{,}905.1$ cm^{-1}. Since none of the other bands unrelated to the main system could be arranged in a second progression consistent with the first, vibrational data for the initial state are lacking.[20] For the final state, we find: $\omega_e'' = 1271$ cm^{-1}, $x_e''\omega_e'' \leqq 4$ cm^{-1}.

Rotational Analysis

It was at first thought that the lower state of this system was the same as that of the main system, since the two values of ω'' concerned are almost identical. High dispersion photographs showed, however, that the line-spacings in the neighborhood of the origins of these new bands were so small that states of considerably lower B-values must be involved. Although we have been unable to resolve the first few R lines and find the origin of any of the bands, we have succeeded in obtaining for both branches of the two bands (0,1) and (0,2)[21] numbering systems which are correct *relatively*,[22] though perhaps in error *absolutely* by one or two units. The assignments adopted are well-suited not only to the individual bands, where practically all of the irregularities are ascribed to the upper state, but also to the relationships which must exist between the two bands. For, over the available

Table IX. *The second system bands (0,1), (0,2).*

(0,1) λ2587.327				(0,2) λ2674.464		
$P(J)$ cm^{-1}	$R(J)$ cm^{-1}	$\Delta_2F'(J)$ cm^{-1}	J	$P(J)$ cm^{-1}	$R(J)$ cm^{-1}	$\Delta_2F'(J)$ cm^{-1}
38631.18			2	37372.31s		
29.46	38638.38	8.92	3	70.57		
27.36	38.13	10.77	4	68.69	37379.57r	10.88
24.95	37.32	12.37	5	66.38	78.81r	12.43
22.31	36.52	14.21	6	63.79	77.94	14.15
19.33	35.30	15.97	7	60.95s	76.95	16.00
16.06	33.87	17.81	8	57.89	75.66	17.77
12.53s	32.28	19.75	9	54.51	74.10	19.59
08.94	30.36	21.42	10	50.95s	72.31s	21.36
05.02	28.19	23.17	11	47.19	70.33	23.14
00.94	25.88	24.94	12	43.29	68.21	24.92
38596.80	23.34	26.54	13	39.32	65.87	26.55
92.60	20.68	28.08	14	35.27	63.44	28.17
88.40	17.92	29.52	15	31.33	60.95s	29.62
84.22	15.23	31.01	16	27.41	58.33	30.92
80.21	12.53s	32.32	17	23.58	55.81	32.23
76.19	09.85	33.66	18	19.90	53.39	33.49
72.38	07.19	34.81	19	16.30	50.95s	34.65
68.65s	04.69	36.04	20	12.82	48.77	35.95
65.05	02.13	37.08	21	09.44s	46.54	37.10
61.41	38599.97	38.56	22	06.22s		
57.59			23	02.71s		

r = resolution incomplete; s = superposition of another line.

[19] Here we postulate violation of Kronig's restriction forbidding intermultiplicity perturbations, as did Rosenthal and Jenkins (reference 16) in the case of the analogous CO perturbations. This could be avoided by assuming that the two perturbations in a single branch are related to different vibrational levels of the interacting state, were it not for the fact that the ω's of the states involved are almost identical.

[20] The main system would in any case obscure all but the strongest and most favorably situated of these second system bands.

[21] It is perhaps confusing that the (0,1) and (0,2) bands of *both* systems are considered in detail.

[22] We assume here that the common level is the upper one, as seems most probable from a comparison of the "non-common level" double-differences required by the alternate hypotheses.

J-value range (3 to 23) data of these bands require (well within the limits of experimental accuracy) identical upper state double differences. These $\Delta_2F'(J)$ values, as well as the wave numbers of the lines themselves, are included in Table IX, and indicate a perturbation near $J'=17$. Rough extrapolations give: $B'(0)=0.43$ cm^{-1}, $B''(1)=0.60$ cm^{-1}, $B''(2)=0.58$ cm^{-1}, with an error of perhaps 0.03 cm^{-1} in each case.

Comparisons

Although the two systems of CS possess almost identical ω'' values, the two B'' values concerned *differ* by about 25 percent. It is likewise noteworthy that $^1\Sigma\rightarrow{}^1\Sigma$ transitions have not been found in PN or SiO, and that the extensive spectrum of CO contains no systems of this type not involving the ground state.

Other Bands

Besides the bands of the two systems already considered, there are a number of weaker bands (some with, some without Q heads) whose intensities appear independent of the amount of impurities present in the source, and which are probably members of additional CS systems. The strongest of these have heads at λλ2721.5, 2735.0, 2813.9, 2912.1 and 3623.6 (quite intense).

General Considerations

The strength of the main system bands, their apparent freedom from perturbations of the lower $^1\Sigma$ state, and their close analogy with the bands of the CO 4th positive system, suggest that the lower level is the ground state ($x^1\Sigma$) of the CS molecule. Similarly, the upper level is probably the lowest $^1\Pi$ level, and lies somewhat above the perturbing state $^3\Pi$.

The positions of the levels of the second system, $C^1\Sigma\rightarrow B^1\Sigma$, have not been fixed with respect to the ground state $x^1\Sigma$, but transitions from these states to those of the main system may produce some of the residual uncorrelated bands. Much longer exposures would permit rotational analyses of some of the weak, unclassified bands.

It should be emphasized that the perturbations in the $C^1\Sigma$ state are definitely unrelated to those found in the $^1\Pi$ state.

Several chemical investigations of the CS molecule have been made, but without definite conclusions regarding the stability of unpolymerized, gaseous CS. Dewar and Jones,[5] for example, believed that the dissociation: $CS_2\rightarrow CS+S$ occurred in the discharge, and that the resulting CS, after existing for a short time as a gas, polymerized to form a brown deposit. More recently, Klemenc[23] concluded that the primary process is formation of excited CS_2 molecules which (at all but liquid air temperatures) dissociate on striking the walls of the tube. He found no evidence of the gaseous CS.

In our investigation, however, we have obtained such intense and prolonged emission after admitting but very minute quantities of CS_2 that we must assume that at very low pressures, CS molecules do exist in the gaseous state, with an appreciable lifetime, and that the solid deposit on the walls continues to evolve CS for protracted intervals.

In conclusion, we wish to thank Professor Harrison for extending to us the use of the 34-ft. grating of the Massachusetts Institute of Technology, and to acknowledge considerable use of the photographic densitometer constructed under a Rumford Grant made to one of us (F. H. C.).

[23] Klemenc, Zeits. f. Electrochemie **36**, 722 (1930).

The Band Spectrum of Ionized Aluminum Hydride[1]

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The Schüler hollow aluminum cathode lamp, containing helium and hydrogen, maintained at 2000 volts d.c., has been used to excite the band spectrum of AlH, which has been photographed with a 21-foot grating spectrograph. Among the new systems appearing there is one with principal head at 3632A which on analysis proves to consist of the (0,0) and (1,1) bands of $a\,^2\Pi$ (regular)$\rightarrow{}^2\Sigma^+$ system due to AlH^+. The $^2\Pi$ state is found to be regular and not inverted as suggested by Holst. The various band constants are obtained and the spin and Λ-doubling compared with theory.

INTRODUCTION

THE band spectrum of AlH has been studied extensively, chiefly by the spectroscopists at Stockholm, using in most cases the Al arc in hydrogen as source. As a preliminary experiment in the use of the hollow cathode lamp of the Schüler type as a source for the excitation of molecular spectra we have photographed the spectrum of AlH. All of the known bands of AlH have been excited with good intensity in this source, as well as several new systems in the ultraviolet, which, however, have also been recently photographed by Holst.[2, 3] Holst has recently reported[3] briefly the results of his analysis of a band at 3632A finding it to be a $^2\Pi$ (inverted)$\rightarrow{}^2\Sigma$ transition in AlH^+ with a coupling constant (A) in the $^2\Pi$ state equal to -39 cm^{-1}. When we discovered this announcement we had just completed an analysis of this system with quite different results. The purpose of this paper is to present our analysis which we believe to be the correct one.

EXPERIMENTAL METHOD

The hollow cathode lamp is of the type described by Schüler,[4] built and placed in a gas-circulating system according to suggestions from Professor Kruger of this laboratory. The discharge, maintained at 2000 volts d.c. by a four-tube hot-cathode mercury rectifier, was carried principally by helium at a few mm pressure to which a small amount of hydrogen was occasionally added. The gas was circulated by a mercury pump; charcoal and chabasite traps were used to remove undesirable gaseous impurities. The intensity of the hydride spectra increased with increasing amounts of hydrogen, but if too much were used the many-lined and continuous spectra of H_2 obscured the *spectra* of the hydride. The proper amount of H_2 and the best pressure of He to give intense hydride spectra without too much background were determined by trial.

This source has several advantages over the low pressure arc: (1) only a little of the element whose hydride is being examined is needed, (2) the metal cathode can be immersed in water, or in liquid air, to reduce the Doppler effect, (3) molecular-ion spectra are probably produced with greater intensity, (4) the source can be operated for hours with little attention.

After preliminary photographs with a Hilger E1 quartz spectrograph the final plates of the bands at 3632A were taken in the first order of a 21-foot grating, 30,000 lines per inch, dispersion 1.3A per mm. Wave-number measurements on one-hour and eight-hour exposures showed excellent agreement. The wave numbers (in vacuum) listed in Table I were calculated from the measurements (mean of two observers) on the eight-hour plate, a reproduction of which appears in Fig. 1.

[1] Paper presented at Washington meeting of American Physical Society, April 27, 1934. Cf. Bulletin **9**, No. 2, p. 20, April 10, 1934.

[2] W. Holst, Nature **132**, 207 (1933); Zeits. f. Physik **86**, 338 (1933).

[3] W. Holst, Nature **132**, 1003 (1933).

[4] H. Schüler, Zeits. f. Physik **59**, 149 (1929).

TABLE I. *Wave numbers arranged in branches.*

For P_1, Q_1 and R_1, $J''=K''+\frac{1}{2}$; for P_2, Q_2 and R_2, $J''=K''-\frac{1}{2}$. Asterisk indicates superposition. d=diffuse, dv=diffuse to violet, dr=diffuse to red.

(0,0) band

K''	I	$^PQ_{12}$	I	P_1	I	Q_1	I	R_1
0					3	27,672.50	0	27,691.25
1			3	27,659.30	8	678.16	7*dv*	709.08*
2			5	651.87	6	683.14	2*d*	727.29
3			6	643.88	6	687.84	5*d*	744.85*
4			6	635.49	6*dv*	692.28*	7	761.76*
5			10*d*	626.73*	8	696.42	3	778.80*
6			9*d*	618.10	8	700.58	10*dr*	795.87*
7			8*d*	609.34	7	704.72	5	812.89*
8			8	600.64	7*dv*	709.08*	4	830.11
9	1	27,592.70	8	592.06	7	713.35	6*d*	847.33*
10	1	584.44	8	583.88	6	717.89	2	864.59*
11	1	576.60	8	575.92	6	722.72	3	882.19
12	1	569.10	6	568.38	3	727.84	5	899.81*
13	0	561.96	6	561.25	6	733.26	2	917.78
14	0	555.37	5	554.58	5	739.01	4	936.03*
15			10*dv*	548.48*	4*d*	744.85*	2*d*	954.32
16			4*d*	542.75	5	751.76	4*d*	973.26*
17			3	537.76	3	758.73	2	991.77*
18			3	533.39	5*d*	766.26*	1	28,011.11
19			4*d*	529.52	1	774.26*	1	030.67
20			2	526.92	2	782.96	1	050.82
21			2*d*	524.43	3	792.20*	3	071.01
22			3*d*	523.14	2	802.03	2*dv*	091.40*
23			3*d*	523.14	5	812.89*	2*d*	113.03
24			1	525.17			2*d*	134.75
25			0	528.05			1	156.53
26								

(1,1) band

K''	I	P_1	I	Q_1	I	R_1
0			2*d*	27,824.02	2	27,842.19
1	3	27,811.49	2	829.48	3	859.94*
2	2	805.09	4	835.11	1	877.87
3	3*d*	798.30	3	840.63	1	895.58
4	3*d*	791.44	5	846.12	2	913.45
5	10*dv*	785.02*	5	851.55*	2	931.56
6	4	778.80*	5	857.43	4	949.77
7	4*d*	771.99*	3	863.55	3	968.35
8	5*d*	766.26*	15	869.97	5*d*	987.56*
9	2	760.50	2	877.16	4	28,006.56*
10	2	755.79	3	884.65	2	026.43
11	5	751.76*	3	892.84	2	046.82
12	2	748.27*	6*d*	901.92*	3*d*	067.58*
13	3	745.83*	3	911.29	2*d*	089.17
14			2	921.58	3*dr*	111.32*
15			1	932.80	1*d*	134.08
16			5	944.97*		
17			2*d*	958.17		
18			1*d*	972.48		
19			5*d*	987.56*		
20			4*d*	28,002.85*		

(0,0) band

K''	I	P_2	I	Q_2	I	R_2
0						
1					1	27,774.26*
2			2	27,748.27	9	785.02*
3	7*dv*	27,709.08*	3	745.83*	10*dr*	795.87*
4	6*dv*	692.28*	4*d*	743.41*	6*d*	807.59
5	2	677.06	8*d*	742.03	6	820.11
6	2	663.43	8*d*	742.03	5*d*	833.36
7	4	650.64	8*d*	742.03	6*d*	847.33*
8	3	638.22	4*d*	743.41*	4	861.64
9	10*d*	626.73*	5*d*	744.85*	2	876.58
10	6	615.51	5	747.05	2*d*	891.95
11	5	605.30	4	749.86	3	907.73
12	5	595.73	4	753.29	2	923.98
13	4	586.85	5	757.23	2	940.45
14	4	578.65	8	761.76*	2*d*	957.51
15	3	571.16	5*d*	766.26*	2*dv*	974.82
16	4*d*	564.42	4*d*	771.99*	2	992.42
17	2*dr*	558.27	4*d*	778.12	1*d*	28,010.67
18	3	552.94	9	785.02*	1	029.02
19	10*dv*	548.48*	3	792.20*	2	048.00
20	2*d*	544.73	3	800.21	3*d*	067.58*
21	1*d*	541.88	1	808.84	4*d*	087.10
22	3	539.89	3*d*	818.30	3	107.14
23	3	538.82*	1	828.43	1*d*	127.98
24	3	538.82*	2	839.37	2*d*	148.68
25			5	851.55*	3*d*	169.93
26			2	864.59*		

(1,1) band

K''	I	P_2	I	Q_2	I	R_2
0						
1					0	27,925.95
2			6*d*	27,901.92*	2	936.65
3	2	27,864.59*	5	899.81*	4	947.88
4	1	850.24	4*dr*	898.48*	4*d*	960.07
5	1	836.78	4*dr*	898.48*	4*d*	973.26*
6	1	824.68	5	899.81*	5*d*	987.56*
7	1	813.74	6*d*	901.92*	4*d*	28,002.85*
8	3	804.04	4	905.23	3	019.09
9	10*dr*	795.87*	3	909.58	3	036.00
10	2	787.68	3	914.77	5*d*	053.77
11	2	781.19	2	920.99	2	072.31
12	6	775.55	3	927.96	2*dv*	091.40*
13	1*d*	771.35	4	936.03*	3*dr*	111.32*
14	3	767.89	5	944.97*	1	132.13
15	5*d*	766.26*	2	954.94	2	153.74
16			2*d*	966.05	2*d*	175.87
17			2*d*	978.32	3	199.18
18			2	991.77*	1*d*	223.97
19			4	28,006.56*		
20			2*d*	022.48		
21			2	039.74		

ANALYSIS OF SPECTRUM. MOLECULAR CONSTANTS

An analysis of the spectrum showed that practically all of the lines of fair intensity could be formed into two bands of six strong branches each, as shown in the Fortrat diagram (Fig. 2) and in the lists of wave numbers (Table I). These bands are accounted for by assuming them to be the (0,0) and (1,1) bands of a $^2\Pi$ (regular)$\rightarrow{}^2\Sigma^+$ transition. That the $^2\Pi$ state is regular (not inverted, as suggested by Holst) is indicated by the presence of $Q_1(1/2)$ and $P_1(3/2)$ in each band. These lines would be absent if the $^2\Pi$ state were inverted. No other assigned band line is superimposed on any of these four lines. The $^PQ_{12}$ "satellite" branch was resolved from the (0,0) P_1 branch beyond $P_1(9\frac{1}{2})$ but became too faint to observe beyond $P_1(14\frac{1}{2})$. This satellite branch enables one to fix the sign and magnitude of the spin doubling in the $^2\Sigma^+$ state. The origins of the (0,0) and (1,1) bands figured from the first lines in the Q branches are:

for the (0,0) band, $\nu_1=27{,}667.8\ \text{cm}^{-1}$ $\nu_2=27{,}760.2\ \text{cm}^{-1}$
for the (1,1) band, $\nu_1=27{,}819.5\ \text{cm}^{-1}$ $\nu_2=27{,}912.5\ \text{cm}^{-1}$.

Since AlH has an even number of electrons its states are singlets and triplets. This band

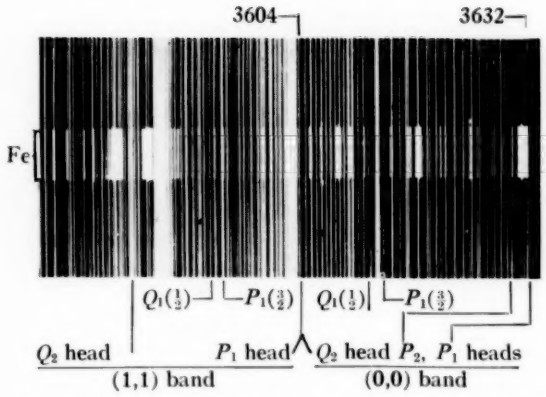

FIG. 1. Part of AlH+ band system ($^2\Pi$(reg)→$^2\Sigma^+$). The presence of the indicated first lines in P_1 and Q_1 branches requires that the $^2\Pi$ state be regular.

spectrum, therefore, is probably due to AlH+. This assumption is strongly supported by the close similarity of this spectrum to the analogous system in MgH. Since on this assignment the configuration of the $^2\Sigma$ state is $(3s\sigma)^2 3p\sigma$, it may be written $^2\Sigma^+$.

$^2\Sigma^+$ state

In the $^2\Sigma^+$ state, for either the F_1 or F_2 states if one neglects spin doubling,

$$F(K)=B_v(K+\tfrac{1}{2})^2+D_v(K+\tfrac{1}{2})^4\cdots$$

$$\Delta_2F(K)=F(K+1)-F(K-1)$$
$$=4B_v(K+\tfrac{1}{2})+8D_v(K+\tfrac{1}{2})^3\cdots$$

to a high degree of approximation. Values of Δ_2F'' are listed in Table II. Δ_2F_2'' and Δ_2F_1'' are the same to within errors of measurement

TABLE II. *Term differences.*
$\Delta_2F''(K'')=R(K''-1)-P(K''+1)$.

K''	(0,0) band: Δ_2F_1''	Δ_2F_2''	(1,1) band: Δ_2F_1''	Δ_2F_2''
0				
1	39.38		37.10	
2	65.20	65.18	61.64	61.36
3	91.80	92.74	86.43	86.41
4	118.47	118.81	110.56	111.10
5	143.66	144.16	134.65	135.39
6	169.46	169.47	159.57	159.52
7	195.23	195.14	183.51	183.52
8	220.83	220.60	207.85	206.98
9	246.23	246.13	231.77	231.41
10	271.41	271.28	254.80	254.81
11	296.21	296.22	278.16	278.22
12	320.94	320.88	300.99	300.96
13	345.23	345.33		323.51
14	369.30	369.29		345.06
15	393.28	393.09		
16	416.56	416.55		
17	439.87	439.48		
18	462.25	462.19		
19	484.19	484.29		
20	506.24	506.12		
21	527.68	527.67		
22	547.87	548.28		
23	566.23	568.32		
24	584.98			

(due largely to superpositions of lines) and thereby indicate a very small spin doubling in the $^2\Sigma^+$ state. In Fig. 3b the average $\Delta_2F''(K'')/4(K''+\frac{1}{2})$ from F_1 and F_2 states is plotted against $K''+\frac{1}{2}$. The intercept at $K''=-\frac{1}{2}$ is the value of B_v''. B_v'' and D_v'' were also obtained by a least squares calculation using values of $\Delta_2F''/4(K''+\frac{1}{2})$ smoothed to the curves in Fig. 3b. From this calculation:

$B_0''=6.564$ cm^{-1} $D_0''=-0.000474$ cm^{-1}

$B_1''=6.166$ cm^{-1} $D_1''=-0.000465$ cm^{-1}.

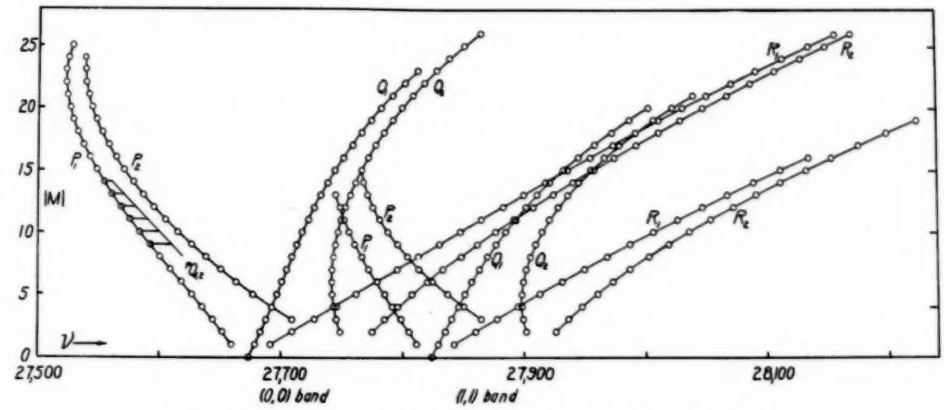

FIG. 2. Fortrat diagram of AlH+ $^2\Pi$(reg)→$^2\Sigma^+$ band system.

From these one obtains:

$$\alpha''=B_0''-B_1''=0.398\ \text{cm}^{-1}$$
$$r_e''=1.60\text{A}$$
$$B_e''=6.763\ \text{cm}^{-1}$$
$$\omega_e''=(4B_e''^3/-D_e'')^{\frac{1}{2}}=1610\ \text{cm}^{-1}.$$

The $^2\Sigma$ spin doubling was obtained from the $^PQ_{12}$ branch since:

$$\Delta\nu_{12}={}^PQ_{12}(K'')-P_1(K'').$$

According to the theory of spin doubling[5] in $^2\Sigma$ states:

$$\Delta\nu_{12}=\gamma(K''+\tfrac{1}{2})$$

where γ is a constant. In Fig. 4c the observed values of $\Delta\nu_{12}$ are plotted against K''. The straight line is $0.056(K''+\frac{1}{2})$, hence $\gamma=0.056$ cm^{-1}.

$^2\Pi$ state

Since, as will be shown, the Λ-type doubling is very small, we assume that the $^2\Pi$ state follows the Hill and Van Vleck equation. Thus:

$$F(J)=B_v\{(J+\tfrac{1}{2})^2-1\pm\tfrac{1}{2}[Y(Y-4)+4(J+\tfrac{1}{2})^2]^{\frac{1}{2}}\}+D_v(J+\tfrac{1}{2})^4 \quad (1)$$

where $Y=A/B_v$, upper sign (+) for F_2, lower sign for F_1. Hence

$$\frac{\Delta_2F(J)}{4(J+\frac{1}{2})}=B_v\left\{1\pm\frac{[Y(Y-4)+4(J+\frac{3}{2})^2]^{\frac{1}{2}}-[Y(Y-4)+4(J-\frac{1}{2})^2]^{\frac{1}{2}}}{8(J+\frac{1}{2})}\right\}+2D_v(J+\tfrac{1}{2})^2. \quad (2)$$

In Fig. 3a values of $\Delta_2F'(J)/4(J+\frac{1}{2})$ are plotted against $J+\frac{1}{2}$ for the $F_2(^2\Pi_{\frac{3}{2}})$ and $F_1(^2\Pi_{\frac{1}{2}})$ levels. From Eq. (2) it is obvious that the mean of the two curves should be given by $B_v+2D_v(J+\frac{1}{2})^2$. By least squares the following constants were found to fit best the mean curve, using values of $\Delta_2F/4(J+\frac{1}{2})$ for $J>5$, because of the uncertain behavior at small J:

$$B_0'=6.727\ \text{cm}^{-1}\quad D_0'=-0.000414\ \text{cm}^{-1}$$
$$B_1'=6.479\ \text{cm}^{-1}\quad D_1'=-0.000409\ \text{cm}^{-1},$$

whence

$$B_e'=6.851\ \text{cm}^{-1},\quad r_e'=1.58\text{A},\quad \omega_e'=1753\ \text{cm}^{-1}.$$

On account of inaccuracy in D_v' and D_v'', values of ω_e' and ω_e'' computed as described are not very reliable. The difference between origins of the (0,0) and (1,1) bands is, however, equal to $\omega_e'-\omega_e''$ to within a few cm^{-1}.

The computation of B_e' does not depend upon the magnitude of the term to the one-half power in Eq. (1), but only upon the fact that $\Delta_2F_2/4(J+\frac{1}{2})$ and $\Delta_2F_1/4(J+\frac{1}{2})$ are symmetrically above and below $[B_v+2D_v(J+\frac{1}{2})^2]$.

The next step was to choose the best value of A. From Eq. (1):

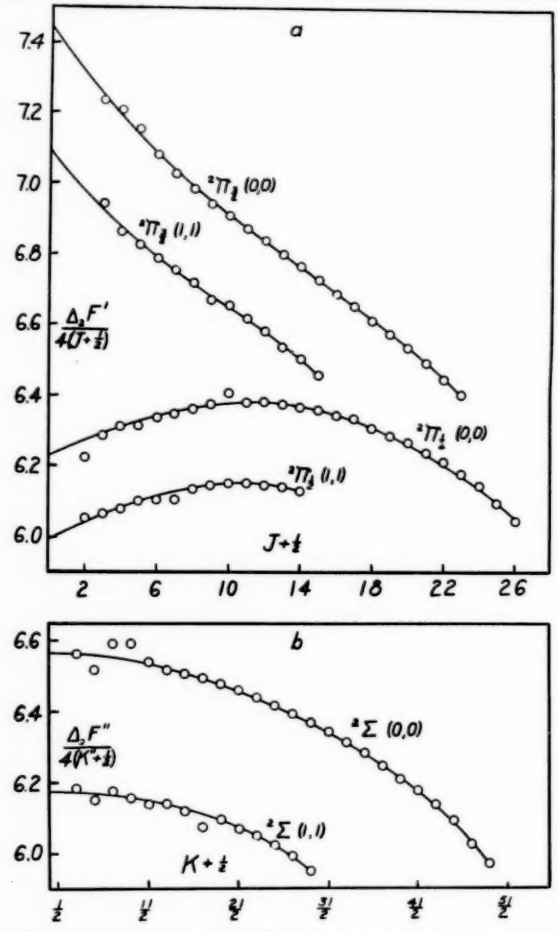

FIG. 3. Values of $\Delta_2F/4(J+\frac{1}{2})$ for all observed states. (a) $^2\Pi$, (b) $^2\Sigma$. Intercepts at left give approximate values of B.

[5] The discussion of spin and Λ-type doubling in this paper is based on the account of these effects given in
[a] R. S. Mulliken, Rev. Mod. Phys. **3**, 89–155 (1931).
[b] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

$$\Delta\nu_{21}(K) = F_2(K) - F_1(K) = B_v\{(2K+1) - \tfrac{1}{2}[Y(Y-4)+4(K+1)^2]^{\frac{1}{2}} - \tfrac{1}{2}[Y(Y-4)+4K^2]^{\frac{1}{2}}\}.$$

By trial it was found that $A = 108$ cm^{-1} gave the solid curve in Fig. 4b in good agreement with observed points obtained from:

$$\Delta\nu_{21}(K') = Q_2(K'') - Q_1(K'') - 0.056(K''+\tfrac{1}{2}),$$

the last term correcting for spin doubling in the lower state. Equally good agreement is obtained in the (1,1) band. Thus the Hill and Van Vleck relation accurately describes the behavior of the $^2\Pi$ state over a wide range of values of K.

Λ-type doubling

Holst based his conclusion that the $^2\Pi$ state was inverted on the Λ-type doubling. The values of this splitting ($\Delta\nu_{dc}$) in the (0,0) and (1,1) bands are given in Table III and plotted in Fig. 4a for the (0,0) band. The Λ-type doubling is so small that errors of measurement make it appear quite erratic (four lines are involved in computing each point). It is doubtful if any conclusion can be drawn as to the nature of the state from the behavior of the doubling, but its trend, if anything, supports our assignment. Thus the theory for regular $^2\Pi$ states indicates that $\Delta\nu_{dc}$ for the $^2\Pi_{\frac{1}{2}}$ state should be zero at the origin, then negative with increasing J, and finally rise to positive values, while for the $^2\Pi_{\frac{3}{2}}$ state $\Delta\nu_{dc}$ should rise slowly from zero at small J. The theoretical values of the Λ-type doubling constants (p and q) calculated according to Van Vleck's theory as formulated by Mulliken and Christy,[5b] were found to be considerably larger than the observed splitting requires. This is, however, the behavior of these constants for

TABLE III. Λ-*type doubling.*
$\Delta\nu_{dc}(J+\frac{1}{2}) = \frac{1}{2}[\Delta\nu_{dc}(J) + \Delta\nu_{dc}(J+1)]$.

$J+\frac{1}{2}$	(0,0) band $\Delta\nu_{1dc}(^2\Pi_{1/2})$	$\Delta\nu_{2dc}(^2\Pi_{3/2})$
1	−0.05	
2	−0.18	0.00
3	+0.09	−0.54
4	+0.28	−0.39
5	−0.10	−0.26
6	−0.05	−0.03
7	−0.05	+0.06
8	−0.18	+0.06
9	−0.13	+0.09
10	−0.02	+0.17
11	+0.05	+0.16
12	0.00	+0.16
13	−0.02	+0.06
14	+0.05	+0.38
15	+0.32	+0.50
16	+0.23	+0.29
17	+0.27	+0.24
18	+0.06	+0.14
19	+0.19	+0.16
20	+0.05	+0.20
21	−0.04	−0.08
22	−0.19	−0.38
23		−0.50

$J+\frac{1}{2}$	(1,1) band $\Delta\nu_{1dc}(^2\Pi_{1/2})$	$\Delta\nu_{2dc}(^2\Pi_{3/2})$
1	+0.09	
2	0.22	−0.25
3	0.22	0.09
4	0.14	0.06
5	0.40	0.18
6	0.69	0.22
7	0.39	−0.13
8	0.55	+0.08
9	0.47	−0.34
10	0.28	0.40
11	0.35	0.50
12	0.17	0.62
13	0.10	0.89
14		0.76

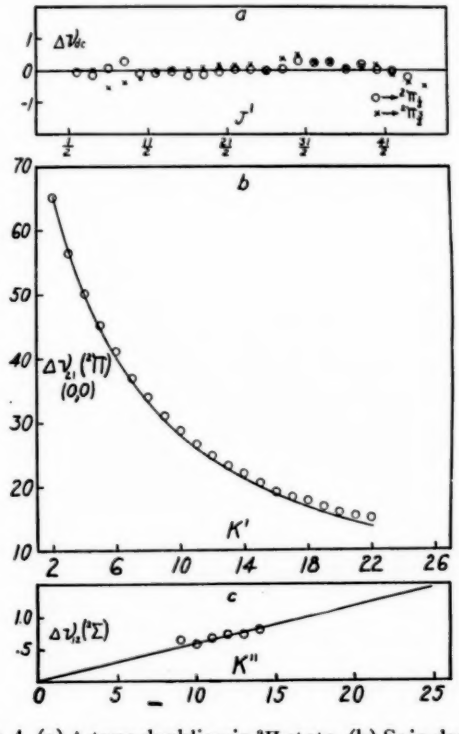

FIG. 4. (a) Λ-type doubling in $^2\Pi$ state. (b) Spin doubling in $^2\Pi$ state, (0,0) band. Observed points $Q_2(K'') - Q_1(K'') - 0.056(K''+\frac{1}{2})$. Solid curve from Hill and Van Vleck formula (Eq. (1)). (c) Spin doubling in $^2\Sigma$ state. Observed points given by $^PQ_{12}(K'') - P_1(K'')$. Solid line drawn to fit observed points, equivalent to 0.056 $(K''+\frac{1}{2})$.

other similar molecules (for example, MgH), according to the survey made by Mulliken and Christy.[5b]

Electronic configuration. Comparison with MgH

A comparison of constants (Table IV) of AlH^+ and the "isoelectronic" molecule MgH strongly indicates that the AlH^+ system at 3632A is the analog of the well-known $^2\Pi$ (regular)$\rightarrow{}^2\Sigma^+$ system of MgH with (0,0) head at 5211A. The correspondence is evident especially in the ratio of electronic coupling coefficients in molecule and parent atom. Mulliken[6] has shown that the $\Lambda\Sigma$ coupling coefficient (A) in $^2\Pi$ molecular states is in a number of cases about nine-tenths the ls coupling coefficient (a) in the ^3P atomic state from which the $^2\Pi$ state is derived. It seems clear that the AlH^+ spectrum reported in this paper arises, as in MgH, from the transition $\cdots(3s\sigma)^2 3p\pi\ ^2\Pi(r) \rightarrow \cdots(3s\sigma)^2 3p\sigma\ ^2\Sigma^+$.

[6] R. S. Mulliken, Rev. Mod. Phys. **4**, 1–86 (1932).

TABLE IV. *Comparison of AlH^+ with MgH.*

		AlH^+	MgH
$^2\Sigma$ state:	ω_e	1610 (calc.)	1494 (obs.)
	r_e	1.60A	1.73A
Spin doubling	γ	0.056	very small
$^2\Pi$ state:	ω_e	1753 (calc.)	1604 (obs.)
	r_e	1.58A	1.68A
Λ-doubling	p	~0.03	0.04
	q	very small	0.002
^3P atomic "a":	a	125.1	40.4
Molecular	A	108.	35.
A/(atomic a)		0.86	0.86
Molecular	ν_0	27,714.	19,310.
$^3P_0 - {}^1S$ (atomic)		37,392. (Al II)	21,851. (Mg I)

Data for MgH from references 5b and 6. All constants (except r) in terms of cm^{-1}.

Pure Rotation Spectrum of the HCl Flame

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(Received April 17, 1934)

Pure rotation lines for $j=17$ to 33 of the emission spectrum of the HCl flame are measured with a KBr prism. The following empirical formulae are determined to represent two series of lines measured corresponding to pure rotation in the two lowest oscillation states,

$$N=0, \quad \nu=20.9j-0.00185j^3; \qquad N=1, \quad \nu=20.2j-0.00163j^3.$$

The linear coefficients agree satisfactorily with values calculated from the empirical oscillation-rotation formula. Theoretically the two cubic coefficients should be equal. The frequency is strongly influenced by the cubic term for high values of j so that the observed difference between these coefficients is regarded as real.

INTRODUCTION

A STUDY of a prism spectrometer in the far infrared, where available energy, rather than interference effects, limits the resolving power, led to the conclusion that the spectrometer should be able to resolve the rotation structure of absorption bands as well as it is possible to resolve them in the near infrared. In fact the resolving power should be as great or greater than that obtainable with a grating.[1]

Recently synthetic crystals, useful as prism materials (KCl, KBr and KI), have become available. These materials are transparent to greater than 30μ making possible a prism spectrometer for the study of far infrared spectra heretofore studied by reststrahlen technique and gratings.[2] Previously, the transmission limit of NaCl at 15–17μ determined the boundary for prism investigations into the infrared.

A prism spectrometer was constructed in this laboratory for the detailed study of spectra in this new region from 15–30μ. Recent developments in infrared technique were incorporated in this instrument such as high sensitivity thermocouple, large aperture optics, vacuum optical path, preliminary spectral purification by residual ray mirrors and Rubens selectively transparent shutters. These added to the possibilities of obtaining high resolving power in the far infrared. Further details of the features of this spectrometer are given in a previous paper.[3]

The first studies in this new spectral region should naturally be devoted to the problems which are of greatest general interest. The two problems studied and herein reported are the emission spectra of HCl and H_2O and also the atmospheric absorption.

A preliminary calculation shows that HCl molecules are excited by moderate temperatures ($T>500°C$) to quantum states ($j>17$) which would give rise to a pure rotation spectrum, $\lambda<29\mu$. It is easier to get pure rotation spectra of a flame in emission than in the absorption of a heated gas, because of the weakness in total radiation. For this reason the emission spectrum of a hydrogen flame burning in an atmosphere of chlorine was chosen for study. Since this molecule has already been extensively studied in both the near and the far infrared, further contribution to its spectrum is of interest. The first study of the HCl emission spectrum was carried out by Julius in 1888.[4] He determined the position of the fundamental oscillation band. The author is not aware of any subsequent publications on the HCl flame. Recent studies under high dispersion of the emission of CO_2 and H_2O flames in the near infrared have been made by Neunhoeffer.[5]

* National Research Fellow.

[1] John Strong, Phys. Rev. **37**, 1661 (1931).

[2] John Strong, Phys. Rev. **36**, 1663 (1930).

[3] John Strong, R. S. I. **3**, 810 (1932).

[4] W. H. Julius, Arch. Neerl. **22**, 310 (1888).

[5] M. Neunhoeffer, Ann. d. Physik **2**, 334 (1929); **4**, 352 (1930).

His resolution was sufficient to show that it was possible to get the rotation structure from a flame.

The Bunsen flame emission is of interest as a calibration source for this region (15–30μ).

The absorption of water vapor in this region is of importance to meteorology because of the rôle it may play in the transfer of heat by radiation at temperatures from 200 to 300°K.

Apparatus

A lamp wherein hydrogen was burned in an atmosphere of chlorine was designed and constructed by Dr. George C. Munro. This lamp consisted of three parallel fish tail burners, mounted in a vertical tube. A window opposite the fish tail burners was covered with a 1μ lacquer film. The radiations, passing out through the lacquer window, were focussed on the spectrometer slit by a 3″ focus concave silvered mirror. With the exception of about 12″ the entire optical path of the pure rotation radiation of the flame from flame to thermopile was in vacuum. A vertical stream of chlorine completely surrounded the burners. In order to prevent the delicate lacquer film from breaking due to the weight of the chlorine gas an air aspirator created a slightly reduced pressure at the top of the tube. The exhaust gases from the lamp were drawn through a flue by a fan. Here they were much diluted by air and discharged into the atmosphere from the top of the laboratory.

The current generated by the pure rotation spectrum falling on the thermopile[6] was measured with a Leeds and Northrup type H. S. galvanometer. The galvanometer was placed on a vibrationless support.[7] A galvanometer scale at 8 meters distance was read to 1/10 mm with a telescope. No amplifier was used.

Calibration

Calibration wave-lengths were determined by the transmissions of atmospheric CO_2[8] (13.95μ) and CS_2[9] (25.2μ). (See Table I.) For CS_2 radiations from 20–30μ were separated from the total radiation of a globar by two reflections from fluorite. The purity of the spectrum dispersed by the HB_2 prism was further insured by the use of a NaCl shutter. The saturated vapor of CS_2 was retained in a thin cell equipped with 1μ lacquer windows. The cell was removable and the transmission was given by the ratio of "cell in" to "cell out" energies. (See Fig. 1.)

The prism was cut from a synthetic crystal grown by a method described in a former paper. It was cut and polished and figured by J. W. Fecker and Company. The prism, property of the University of Michigan, was kindly loaned to me by Professor Randall for this investigation.

The prism angle was measured on a "student" spectrometer as 28° 20′ 10″. The calibration curve was defined by this datum, the index of KBr at 13.95μ as determined from the smoothed

Table I. *Calibration data.*

λ in μ	M ×10,000	$n_{35°C}$	Gas	λ in μ	M ×10,000
14	4206	1.5141	CO_2	13.95	4190
15	4440	——	CS_2	25.20	7960
16	4692				
17	4963				
18	5254				
19	5564				
20	5895				
21	6248				
22	6620				
23	7015				
24	7432				
25	7871				
26	8332				
27	8820				
28	9340				
29	9890				

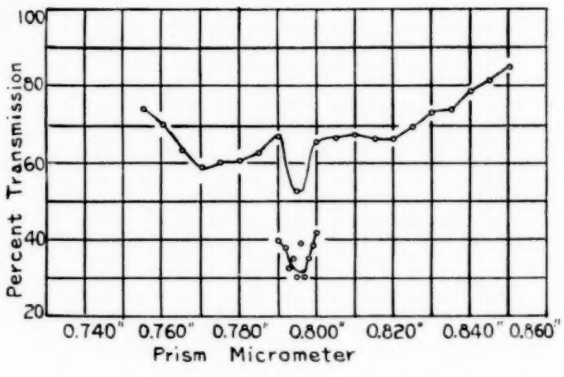

Fig. 1. CS_2 transmission curve for the 25.2μ band.

[6] John Strong, R. S. I. **3**, 65 (1932).
[7] John Strong, Phys. Rev. **37**, 1565 (1931).
[8] Louis Russell Weber and H. M. Randall, Phys. Rev. **40**, 835 (1932).
[9] D. M. Dennison and Norman Wright, Phys. Rev. **38**, 2077 (1931).

data of Korth,[10] the prism micrometer readings at 13.95 and 25.20μ, the fact that 1° prism rotation equals 0.1817″ on the micrometer screw, and the assumption that the ultraviolet terms do not contribute to the dispersion of KBr in this interval.

From these data the following dispersion equation for KBr is obtained in which ultraviolet terms appear in the constant term.

$$n^2 = 4.90435 - 19{,}858(\lambda_0^{-2} - \lambda^{-2})^{-1},$$

where $\lambda_0 = 88.3\mu$ as determined by Barnes.[11]

The relationship between prism micrometer readings, M, and λ is given by the relation:

$$\frac{\sin^2(48° 14' 52'' - M/.1817)}{\sin^2(28° 20' 10'')} = 4.90435 - 19{,}858(7797 - \lambda^2)^{-1}.$$

This relationship is open to criticisms on the ground that the assumption that the ultraviolet terms are essentially constant may not be valid. Furthermore the index for 13.95μ is for 38°C whereas the prism was used at 23°C. It is contended that the errors arising from these sources are insignificant. The data used, with the exception of the index at 13.95μ, were all taken at 23°C. The temperature coefficient of the index of refraction of all known prism materials decreases to very low values at their extreme infrared limit of transmission. In any event the errors introduced would be of second order and should appear only midway between 13.95μ and 25.20μ as well as considerably beyond 25.20μ.

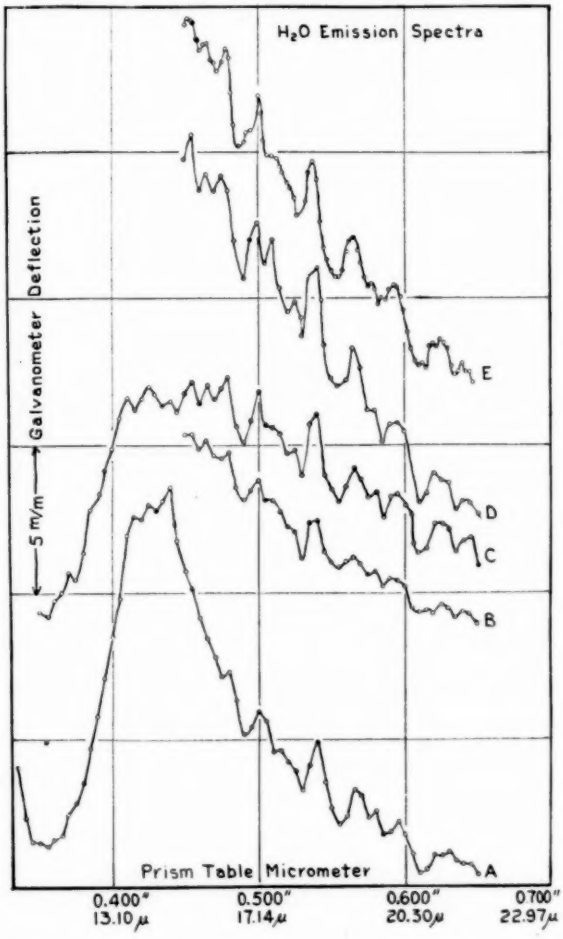

FIG. 2. Emission spectra of Bunsen flame, A, of gas-oxygen flame B and C, and oxy-hydrogen flame, D and E.

[10] K. Korth, Zeits. f. Physik **84**, 677 (1933).

[11] R. Bowling Barnes, Zeits. f. Physik **75**, 723 (1932).

MEASUREMENTS ON H_2O

The new results obtained from measurements of the emission of a Bunsen flame are shown in Fig. 2, curve A and are tabulated in Table II. That these maxima are due to H_2O is indicated by the curves B and C for the emission of H_2 burning from two fish tail burners of the HCl lamp in an atmosphere of air. Curves D and E are for one burner of the lamp with an atmosphere of pure oxygen instead of air as in the above case.

TABLE II.

H_2O emission lines					
M ×1000	λ in μ	M ×1000	λ in μ	M ×1000	λ in μ
413	13.54	500	17.14	578	19.65
425	14.19	510	17.49	593	20.09
440	14.84	525	18.00	616	20.75
452	15.33	538	18.42	620	20.86
464	15.81	565	19.25	630	21.13
478	16.34			642	21.46

Atmospheric absorption lines					
M×1000	735	791	830	862	883
λ in μ	23.81	25.09	25.93	26.61	27.03

Unfortunately the emission of the H_2O flame was never extended beyond 20μ.

The "cell out" measurements on CS_2 give the absorption lines given in Table II. These atmospheric lines are presumably due to H_2O.

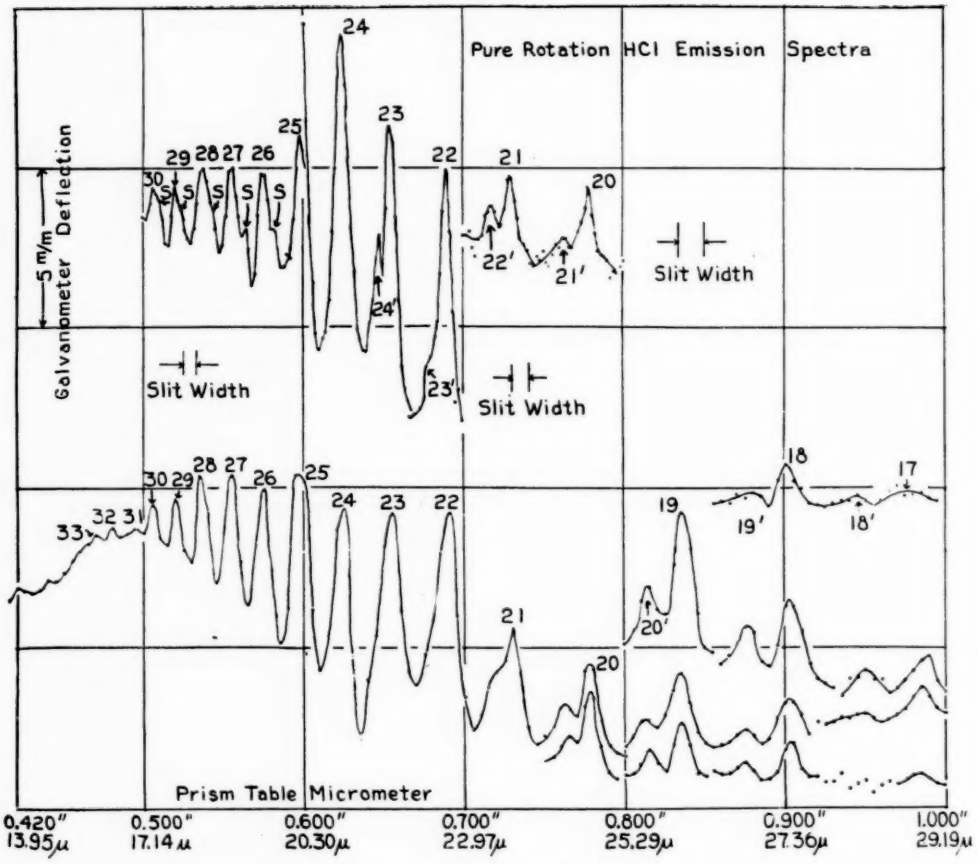

FIG. 3. Pure rotation HCl emission spectra.

MEASUREMENTS ON HCl

Measurements of the HCl rotation spectrum were made with an NaCl shutter beyond 24μ and metallic shutter below 24μ. As previously stated, the total emission of the flame was small (not perceptible to the hand) so the two fluorite reflections, used before with a Globar source, were unnecessary.

Results of all measures on HCl are plotted in Fig. 3 and given in Table III; about 50 lbs. of chlorine were boiled away to make these measures. The level of liquid chlorine was indicated by the frost which formed on the outside of the tank.

It is noticed that there are three series of lines. Those lines represented by the quantum numbers 17 to 33, those represented by the primed quantum numbers 18′ to 24′ and those represented as satellites of the lines 26S to 30S.

CLASSIFICATION OF HCl LINES

The difference between two energy states of rotation in the zero oscillation state is given by the relationship

$$W_0(j+1)-W_0(j-1)=\nu^+_{osc}(j-1)$$
$$-\nu^-_{osc}(j+1)=\nu_{rot}(j-1)+\nu_{rot}(j).$$

Using the oscillation-rotation data of Colby, Meyer and Bronk[12] we can make the following comparison between the values of this energy difference with that obtained from the data for the first series of pure rotation lines given in Table II. This comparison follows:

j	$\nu^+_{osc}(j-1)-\nu^-_{osc}(j+1)$	$\nu_{rot}(j-1)+\nu_{rot}(j)$	Δ
18	3138.8 − 2429.9 = 708.9	345.6 + 364.6 = 710.2	−1.3∼/cm
19	3148.1 − 2401.2 = 746.9	364.6 + 384.2 = 748.8	−1.9∼/cm

[12] Colby, Meyer and Bronk, Astrophys. J. **57**, 7 (1923).

The agreement to $1.3\sim$/cm for $j=18$ and to $1.9\sim$/cm for $j=19$ confirms the classification of the lines $j=17$ to $j=33$ as pure rotation lines of HCl in the ground oscillation state.

The corresponding relationship for the first oscillation state, $N=1$, is

$$W_1(j+1)-W_1(j-1)=\nu^+_{osc}(j)-\nu^-_{osc}(j)$$
$$=\nu_{rot}(j-1)+\nu_{rot}(j).$$

The comparison of the data of Colby, Meyer and Bronk with the second series of HCl lines is as follows:

j	$\nu^+_{osc}(j)-\nu^-_{osc}(j)$	$\nu_{rot}(j-1)+\nu_{rot}(j)$	Δ
18	$3155.4-2429.9=725.5$	$354.0+371.9=725.9$	$0.4\sim$/cm
19	$3161.5-2401.2=760.3$	$371.9+391.1=763.0$	$2.7\sim$/cm

The agreement to $0.4\sim$/cm for $j'=18$ and to $2.7\sim$/cm for $j'=19$ confirms a classification of the lines $j'=18$ to $j'=24$ as pure rotation lines of HCl in the state of oscillation $N=1$.

The five satellites designated by S, are unexplained. They are not due to pure rotation in the state $N=1$ since they do not agree with the positions predicted by an empirical equation representing the lines $j'=18$ to $j'=24$. They are not due to rotation isotope effect. This effect is very small for pure rotation as the chlorine atom is very near the center of rotation and the moment of inertia is consequently insensitive to small changes of its mass. For $j=27$ the distance between HCl_{37} and HCl_{35} is about $1\sim$/cm whereas the displacement of the satellite from the line $j=27$ is about $8\sim$/cm.

It would be inconsistent with the expected distribution in the energy states to classify these lines as pure rotation for the state $N=2$. One would expect more than only these five lines to appear.

They are not easily described to instrumental causes (as they might be if they were measured with a grating rather than a prism). The data are not sufficient to allow a precise determination of their wave-lengths on account of their nearness to the lines $j=26-j=31$.

Empirical Equations

The fourteen lines $j=17$ to $j=33$ were fitted to an equation of the form

$$\nu=Aj-Bj^3.$$

Table III. *Pure rotation HCl emission lines.*

j	M ×1000	λ in μ	ν observed in $\sim$/cm	ν calculated in $\sim$/cm	$\Delta\nu$ in $\sim$/cm
$N=0$					
17	985	28.93	345.6	346.2	−0.6
18	904	27.43	364.6	365.4	−0.8
19	835	26.03	384.2	384.4	−0.2
20	778	24.79	403.4	403.2	0.1
21	730	23.69	422.1	421.8	0.3
22	690	22.72	440.1	440.3	−0.2
23	655	21.82	458.3	458.2	0.1
24	624	21.08	474.4	476.0	1.6
25	598	20.23	494.3	493.6	0.7
26	575	19.56	511.2	510.9	0.3
27	555	18.95	527.7	527.9	−0.2
28	538	18.42	542.9	544.6	−1.7
29	520	17.82	561.1	561.0	0.1
30	506	17.35	576.4	577.1	−0.7
31	495	16.96	589.6	592.8	−3.2
32	480	16.41	609.4	608.2	1.2
33	470	16.04	623.4	623.2	0.2
$N=1$					
18′	949	28.27	354.0	354.1	−0.1
19′	876	26.89	371.9	372.6	−0.7
20′	813	25.57	391.1	391.0	0.1
21′	763	24.45	409.0	409.1	−0.1
22′	718	23.41	427.2	427.2	0
23′	680	22.48	444.8	444.8	0
24′	648	21.62	462.5	462.1	0.4
Satellites					
26S	582	19.76	506.1		
27S	564	19.23	520.0		
28S	544	18.61	537.3		
29S	524	17.95	557.1		
30S	510	17.49	571.7		

This was easily done by plotting ν/j *versus* j^2 and drawing a straight line through the points. A is determined by the intercept of this line and B is determined by its slope.

A similar procedure was followed for the lines $j'=18$ to $j'=24$. The equations obtained were

$$\text{for } N=0 \quad \nu=20.9j-0.00185j^3 \text{ and}$$
$$\text{for } N=1 \quad \nu'=20.2j'-0.00163j'^3.$$

The data for lines $j=24$, 28 and 31 were not used in this determination. The calculated and observed frequencies are given in Table III together with discrepancies. Discarding the three lines just mentioned the average deviation for a single line from the calculated values is $0.4\sim$/cm. This is a measure of the accuracy of the determination of a single line.

Discussion

The blend $\frac{3}{4}HCl_{35}+\frac{1}{4}HCl_{37}$ gives a line for $j=27$ about $0.2\sim$/cm displaced from the line of pure HCl_{35}. Since this is small compared to

the 0.4∼/cm accuracy no analysis was carried out to determine two formulae (for $N=0$) for the two important isotopic constituents of the chlorine. More precise measures of this spectrum should, however, give data which would allow this isotope effect to be determined because the half-line breadth is calculated to be of the order of 1∼/cm.

From the formula representing the lines of the oscillation-rotation spectrum it is possible to calculate the coefficient of the pure rotation spectrum from the relationship (Linear coefficient+Square coefficient)$_{\text{oscillation}}$=(Linear coefficient)$_{\text{pure rotation}}$. From the data of Colby, Meyer and Bronk, we get good agreement with the pure rotation coefficient.

$$20.598+0.301=20.899$$

(from oscillation-rotation lines).

This value, 20.899, agrees better with the empirical value 20.9 than with Czernys' value 20.794.[13]

The difference between the linear coefficient, A, for $N=0$ and A for $N=1$ should be twice the square coefficient of the oscillation-rotation formula. Here we have

$$20.9-20.2=0.7 \text{ (observed) and}$$
$$2\times.3=0.6 \text{ (calculated).}$$

The cubic term from the Colby, Meyer and Bronk data is 0.002056 as compared to 0.00185 for $N=0$ and 0.00163 for $N=1$ and 0.00164 from Czerny's measurements. Since the determination of the cubic term is more accurate when determined for larger values of j the value 0.00185 for $N=0$ and 0.00163 for $N=1$ are therefore to be considered most reliable.

In conclusion I wish to acknowledge my appreciation of the help I have obtained from Professor R. A. Millikan and Professor W. V. Houston.

[13] M. Czerny, Zeits. f. Physik **53**, 317 (1929).

The Nuclear Moment of Tl

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(Received April 27, 1934)

The value of $\psi^2(0)$ for the $7s$ state of Tl I is calculated relativistically and compared with the value determined from the formula $\psi^2(0)=Z_i Z_0^2/\pi a_H^3 n_0^3$. With the experimental value of the hyperfine structure splitting of this level, the magnetic moment of the Tl nucleus is found to be: $1840g \leqq 2.7$. The f values corresponding to the transitions $p_{3/2}s_{1/2}$ and $p_{1/2}s_{1/2}$ are also determined and are found to be in agreement with experiment when the effect of a perturbation is taken into account.

INTRODUCTION

IN order to calculate nuclear magnetic moments from the hyperfine structure splittings of s levels, one needs the value of $\psi^2(0)$, the probability of finding the s electron in a unit volume near the nucleus. For this calculation, various writers[1, 2, 3] have used the formula $\psi^2(0)=Z_i Z_0^2/\pi a_H^3 n_0^3$ where Z_i is the effective nuclear charge in the inner part of the orbit, a_H the Bohr radius, Z_0 the effective charge in the outer part of the orbit, and n_0 the effective quantum number, defined by equating the term value energy to $-RZ_0^2/n_0^2$. An accurate numerical calculation of $\psi^2(0)$ provides a test for the validity of this semi-empirical formula. The results of several such calculations were reported in reference 2; in some of these the agreement with the formula was good, but in other cases poor. It seemed worth while therefore, to carry out some further calculations.

THEORY

The $7s$ state of Tl I with the term energy 22,787 cm^{-1} was used. The method followed has been outlined by Breit[4] and will be discussed only briefly here. Radial functions closely related to Gordon's F and G are used, and the equations they satisfy are:

$$d\phi_1/dr - j'\phi_1/r = [(2\pi/\Lambda)(1-E/mc^2)+V]\phi_2,$$

$$d\phi_2/dr + j'\phi_2/r = [(2\pi/\Lambda)(1+E/mc^2)-V]\phi_1,$$

$\Lambda=h/mc$, E is the energy, V the potential energy, and for s terms $j'=-1$. The solutions of these equations are used to evaluate

$$\psi^2(0) = -\frac{2}{\Lambda}\frac{\int_0^\infty(\phi_1\phi_2/r^2)dr}{\int_0^\infty(\phi_1^2+\phi_2^2)dr}.$$

With the Fermi-Thomas field for small values of $r(r<0.06a_H)$ solutions may be obtained in terms of hypergeometric functions, and these suffice for calculating $\int_0^\infty(\phi_1\phi_2/r^2)dr$ since the integrand falls off very rapidly with r. The calculation of the normalization integral $\int_0^\infty(\phi_1^2+\phi_2^2)dr$ is simplified by the fact that ϕ_1^2 may be neglected in comparison with ϕ_2^2 throughout the whole range of r which contributes to the integral.

A solution for $\phi_2(r>0.06a_H)$ is obtained by using the Wentzel-Kramers-Brillouin method in a slightly modified form. This leads to a sinusoidal solution which may be joined to the hypergeometric series solution at the first node, and an exponential solution for large r. The sine and exponential solutions do not join, but the gap may be bridged by using the Schroedinger ψ function, since for large values of r, ϕ_2 behaves as $r\psi$. By making a slight change in the field it was possible to join the Schroedinger solution to the sinusoidal W. K. B. solution at its last node. The exponential solution for large values of r was then seen to be identical with the Schroedinger solution in that region.

[1] Pauling and Goudsmit, *Structure of Line Spectra*.
[2] G. Breit, Phys. Rev. **42**, 348 (1932).
[3] McLennan, McLay and Crawford, Proc. Roy. Soc. **A133**, 652 (1931). For modifications of formula see Fermi and Segrè, Zeits. f. Physik **82**, 729 (1933).
[4] G. Breit, Phys. Rev. **38**, 463 (1931).

The Fermi-Thomas field was first changed so that the phase integral was 5.75π in accordance with Kramers' rule. This was accomplished by making the field purely Coulomb beyond a point $r=r_0$, this point being determined by trial. In order to remove the resulting discontinuity in the potential at r_0, the difference between the Fermi-Thomas and Coulomb values at r_0 was subtracted from all values between r_0 and the origin. This process still leaves a break in the slope of the potential function at r_0 which may be smoothed out graphically. No reasonable smoothing out of this break made any difference in the calculations considered. In the final field used, the value of the phase integral had to be increased slightly (about 1 percent) over the value 5.75π. A comparison of this field with that used by Breit[4] showed the two to be practically identical. Thus the same field is in agreement with the experimentally determined energies of $p_{3/2}$, $p_{1/2}$, $s_{1/2}$ states.

The result of this relativistic calculation is $\psi^2(0)=3.7(8)\times10^{25}$ cm^{-3}. The value from the formula $\psi^2(0)=Z_iZ_0^2/\pi a^3{}_H n_0^3$ is 1.7×10^{25} cm^{-3} but the relativity correction must still be applied to this. According to Racah[5] this correction factor is 2.31, so that $\psi^2{}_{rel.}(0)=3.9\times10^{25}$ cm^{-3}.

The agreement between these two results is as good as could be expected. It is difficult to determine the probable error of this calculation; 10 percent is a rough estimate. Racah has also calculated $\psi^2(0)$ for this state, obtaining a value 11.3×10^{25} cm^{-3}, which is three times as large as that found here.

Calculation of f Values

Knowing the values of ϕ_2 for $p_{3/2}$, $p_{1/2}$, $s_{1/2}$ states, one can calculate the f values for the transitions $p_{3/2}$, $s_{1/2}$ and $p_{1/2}$, $s_{1/2}$ which we denote by f_{5350} and f_{3776}. The f values are given by

$$f_{ji}=(8\pi^2 m\nu_{ji}/3h)\sum(m_j)\{|x_{m_j,\,m_i}|^2+|y_{m_j,\,m_i}|^2+|z_{m_j,\,m_i}|^2\}.$$

For the calculation of matrix elements $x_{m_j,\,m_i}$ etc., only the radial function ϕ_2 is used, but the angular dependence must be taken into account. This calculation gives $f_{5350}=0.146$; $f_{3776}=0.114$ as compared with the measured[6,7] values 0.076 and 0.08, respectively.

These discrepancies may be explained by the presence of a perturbing configuration. According to Fermi and Segrè[8] the configuration $6s^26p$ which gives rise to the p terms discussed above is perturbed by the configuration $6s6p7s$ which lies about 7 volts above it. They find that they may use

$$\psi=0.96\psi_0-0.22\psi_1+0.18\psi_2+0.03\psi_3,$$

where ψ is the perturbed eigenfunction for the state $(p_{3/2})_{3/2}$ and

$$\psi_0=\{6s\ S_{1/2},\ 6s\ S_{-1/2},\ (6p)_1\ S_{1/2}\},$$
$$\psi_1=\{6s\ S_{-1/2},\ 7s\ S_{1/2},\ (6p)_1\ S_{1/2}\},$$
$$\psi_2=\{6s\ S_{1/2},\ 7s\ S_{-1/2},\ (6p)_1\ S_{1/2}\},$$
$$\psi_3=\{6s\ S_{1/2},\ 7s\ S_{1/2},\ (6p)_1\ S_{-1/2}\}.$$

These functions are supposed to be antisymmetrized by writing them as determinants with the proper normalization factor.

In order to investigate the effect of this perturbation on f_{5350}, approximate values of ϕ_2 for the $6s$ electron were obtained. The field used was the same as that for the $7s$ electron, and the energy for $6s$ was determined to fit this field. Since no experimental energy for $6s$ was available, this seemed to be the best procedure to adopt. The $7s$ term used in this calculation arises from $6s^27s$ and we represent $(s_{1/2})_{1/2}$ by $\{6s\ S_{1/2},\ 6s\ S_{-1/2},\ 7s\ S_{1/2}\}$. Since the angular dependence for all s terms is the same, the effect of this perturbation is to change only integrals over the radial variable. The perturbation reduces the value of f_{5350} to 0.073, which agrees with the measured value, 0.076 better than could be expected from the accuracy of the calculation.

This perturbation also affects the value of f_{3776} which involves the $p_{1/2}$ state. We represent the unperturbed wave function for $(p_{1/2})_{1/2}$ by

$$(3)^{-\frac{1}{2}}(\phi_0'-(2)^{\frac{1}{2}}\phi_0''),$$

where

$$\phi_0'=\{6s\ S_{1/2},\ 6s\ S_{-1/2},\ (6p)_0\ S_{1/2}\},$$
$$\phi_0''=\{6s\ S_{1/2},\ 6s\ S_{-1/2},\ (6p)_1\ S_{-1/2}\}.$$

[5] G. Racah, Zeits. f. Physik **71**, 431 (1931).

[6] Det. Kgl. Danske Videnskab. Selskab. Mathem. Meddeleser **7**, 12 (1926).

[7] Prokofjew and Solovjev, Zeits. f. Physik **48**, 276 (1928).

[8] Fermi and Segrè, Reale Accademia D'Italia **IV**, 131 (1933).

The radial integrals involved in the calculation of the coefficients for the perturbed $(p_{1/2})_{1/2}$ function, which we denote by ϕ, can be reduced to those evaluated by Fermi and Segrè, and

$$\phi = 0.97\phi_0 + 0.13\phi_1 - 0.11\phi_2 - 0.15\phi_3 + 0.09\phi_4,$$

where

$$\phi_1 = \{6s\ S_{-1/2},\ 7s\ S_{1/2},\ (6p)_1\ S_{-1/2}\},$$

$$\phi_2 = \{6s\ S_{-1/2},\ 7s\ S_{1/2},\ (6p)_0\ S_{1/2}\},$$

$$\phi_3 = \{6s\ S_{1/2},\ 7s\ S_{-1/2},\ (6p)_1\ S_{-1/2}\},$$

$$\phi_4 = \{6s\ S_{1/2},\ 7s\ S_{-1/2},\ (6p)_0\ S_{1/2}\}.$$

The effect of this perturbation is to reduce f_{3776} to 0.059 as compared with the measured value 0.08.

This agreement between calculated and measured intensities indicates that Fermi and Segrè's explanation of the anomalous splitting ratio of $p_{1/2}$ and $p_{3/2}$ in terms of this perturbation must be essentially correct.

The nuclear magnetic moment is given by $g\mu_0 i$. Here μ_0 is the Bohr magneton, i the angular momentum of the nucleus in units of $h/2\pi$, and the g factor may be determined from the hyperfine structure splitting of a given level. The g factor found from Schüler and Keyston's[9] data on the $7s$ level of Tl I is compared with other determinations in Table I.

TABLE I.

	$s_{1/2}$	$p_{1/2}$	Most probable value according to Fermi
1840g	2.7	2.9	2.8

The $6p_{3/2}$ level is perturbed so strongly that one cannot rely on the g value determined from it. The g value for $p_{1/2}$ was calculated by Breit[4] and in this calculation the perturbation of $6s^2 6p$ by $6s6p7s$ was not taken into account. Calculation shows that this perturbation causes an increase in the g value of about 3 percent, but since the perturbed wave function for $p_{1/2}$ cannot be determined accurately, no significance can be attached to this correction.

In conclusion the writer wishes to thank Professor G. Breit for his helpful suggestions regarding this calculation, and for the use of tables of functions for the $6p$ states of Tl.

[9] Schüler and Keyston, Zeits. f. Physik **70**, 1 (1931).

Positive and Negative Thermionic Emission from Columbium

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(Received April 4, 1934)

The positive ion and electron work functions have been determined for well outgassed columbium and found to be for the electrons 3.96 volts with A equal to 57 amp./cm²/degree² and for positive ions 5.52 volts. It has been found that by bombarding the ionization gauge at a high temperature the specimen could be contaminated so as to change the electron work function by about 16 percent. The effect of impurities on the positive ion work function has been studied and it is shown that these will in general cause an increase in this quantity.

IN a series of letters to the editor it has been shown by one of us[1] that certain metals when heated to a sufficiently high temperature will emit positive ions of the metals themselves. It has been known for a long time that all metals when first heated to incandescence will emit positive alkaline ions but as far as the writers have been able to tell the metallic ions have hitherto escaped detection.

These findings have been verified by Smith,[2] who independently noted the emission of ions, which he concluded had a greater mass than the potassium ions, from tungsten. Later[3] he made a qualitative determination of the positive ion work functions for tungsten and molybdenum after determining the mass of the ions. Barnes[4] has extended and verified the results listed above and in addition has repeated Smith's determination of the work function for molybdenum. He obtained a value of 8.12 volts. This is about two volts higher than that obtained by Smith. Both these values are questionable due to insufficient heat treatment of the specimens used.

In the work described below the work functions for the electrons as well as for the positive ions has been determined for columbium, precautions being taken to eliminate spurious effects as much as possible.

EXPERIMENTAL PROCEDURE

An accurate determination of the work function, thermionically, requires that the temperature of the metal under investigation shall be known with considerable accuracy. This is particularly true if a reliable value of the constant A in the thermionic equation is desired.

Since the value of the emissivity used in computing the true temperature from the brightness temperature as determined with an optical pyrometer, may be a function of the outgassing, it was necessary to determine this quantity under good vacuum conditions. Mr. L. V. Whitney made such a determination using the wedge method. The optical pyrometers used followed the design proposed by Fairchild and Hoover.[5] The brightness and true temperatures are listed in Table I.

TABLE I. *Brightness temperature, T_B, and true temperature T_T, for $\lambda = 6690°A$.*

T_B°K	T_T°K	T_B°K	T_T°K
1200	1266	1650	1784
1250	1325	1700	1841
1300	1383	1750	1898
1350	1440	1800	1957
1400	1497	1850	2016
1450	1555	1900	2077
1500	1611	1950	2139
1550	1670	2000	2203
1600	1726		

The first thermionic determinations were made with a two guard ring tube (Fig. 1). G_1G_2 are the guard rings and C the collecting cylinder. Q_1Q_2 are two quartz rods which clamped the collector and guard rings in place. The collector was 25

[1] H. B. Wahlin, Phys. Rev. **34**, 164 (1929); **35**, 653 (1930); **37**, 467 (1931); **38**, 1074 (1931); Nature **123**, 912 (1929).

[2] L. P. Smith, Phys. Rev. **33**, 279 (1929).

[3] L. P. Smith, Phys. Rev. **35**, 381 (1930).

[4] L. L. Barnes, Phys. Rev. **42**, 487, 492 (1932).

[5] Fairchild and Hoover, J. O. S. A. and R. S. I. **7**, 542 (1923).

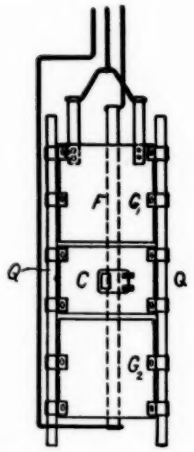

FIG. 1. Diagram of two guard ring tube.

mm in diameter and 25 mm long. The guard rings were about 40 mm long. The filament F, a strip of columbium 15 cm long, 2 mm wide, and 0.05 mm thick was held along the axis of the system of cylinders. The metallic parts of the tube were first heated in a vacuum to a final temperature of about 1300°C by electron bombardment. This heating extended over a period of 200 hours. The cylinders were then transferred to the main experimental tube and this sealed to the vacuum system as soon as possible. In all, the cylinders were exposed to the air for about 24 hours. Care was taken in handling the cylinders after outgassing to avoid contamination which may cause appreciable alkaline ion currents when the metal becomes warm.

The tube was evacuated and baked at a temperature ranging from 300°C to 400°C for a period of 250 hours. During the latter part of this baking the filament was heated to a final temperature of 1700°K. The furnace was then removed and the heating of the filament continued at a temperature of 1900°K for a total period of 1400 hours.

Fig. 2, curve A, shows a plot of $\log_e i - 2\log_e T$ against $1/T$ for electron data obtained after about 700 hours outgassing. As will be noticed, this curve shows a distinct break. The values of the work functions for the two parts of the curve are: for the high temperatures 4.0 volts and for the low temperatures 3.3 volts. With continued outgassing the break diminished until in the final stages it disappeared entirely (curve B). The final value obtained for the electron work function was 3.95 volts. The constant A was found to be 57 amp./cm²/degree², a good check with the theoretical value of 60.2. The value of φ and A given above did not vary during the last 200 hours of heat treatment.

In the tube used in the above determinations the insulation between the cylinders was not sufficiently good to allow accurate measurement of the very small positive ion currents. Therefore the single guard ring tube (Fig. 3) with a loop filament was substituted. In this tube the collector (C) was supported from below and the filament (F) and guard ring (G) was held from a seal at the top. A disk shielded the lower seal from metallic vapor and thus prevented leakage across the glass. The tube was made sufficiently long so that the lower seal could be maintained at room temperature with the filament hot. The ionization gauge used in measuring the pressure was sealed to the evacuating lead about 25 cm from the experimental tube. The baking and outgassing process was approximately the same as for the first tube and extended over a total period of 1600 hours.

The first determinations of the electron work function made after 400 hours outgassing gave a value of 3.5 volts. The break which had appeared with the first specimen was entirely absent. With further outgassing this value rose until after 900 hours it had reached a value of 3.96 volts. The pressure at this time was about 7×10^{-8} mm.

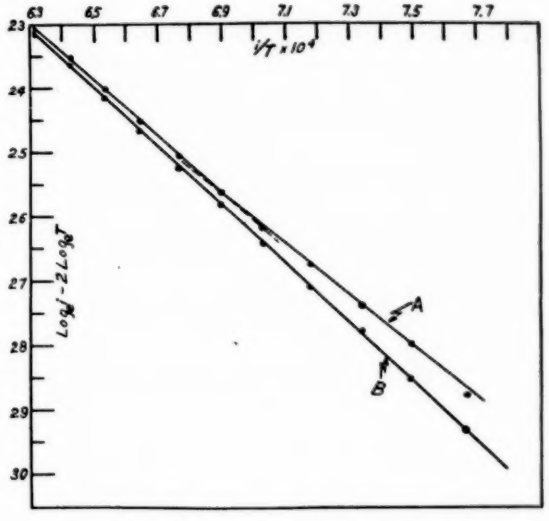

FIG. 2. Plot of $\log_e i - 2\log_e T$ against $1/T$.

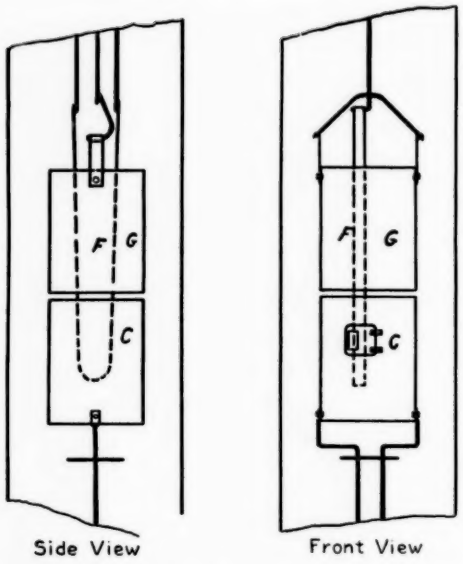

FIG. 3. Diagram of single guard ring tube.

The ionization gauge was then outgassed by bombardment at a temperature higher than that ordinarily used. After this bombardment the break appeared in the Richardson plot. The two values found for φ were 3.9 and 3.4 volts. Further heat treatment of the filament for 100 hours caused the break to disappear and the work function returned to a value of 3.96 volts. This value persisted over a total outgassing time of 1400 hours. In the meanwhile the pressure had dropped to less than 4×10^{-8} mm. A further change in the pressure to a final value of 10^{-8} did not change the results.

POSITIVE ION WORK FUNCTION

After 1400 hours outgassing, determinations of the positive ion work function were made. For this a quadrant electrometer with a current sensitivity of 4×10^{-12} amp./mm was substituted for the galvanometer used in measuring the electron space current. In order to shield the experimental tube from electrostatic effects the glass was given a coating of aquadag which was grounded. This was so satisfactory that air could be blown against the tube to cool it without the electrometer being disturbed.

The initial work function determination between the temperature limits of 2000°K and 2200°K was about 7.9 volts. Between 1800°K and 1950°K, with a higher electrometer sensitivity, a value of 5.4 volts was obtained. A continued flashing of the filament at the higher temperatures caused a lowering of the space current and also a lowering of the high temperature work function until a final value of 5.52 volts was obtained for both temperature ranges.

These values were computed from the equation

$$i=BT\ \text{exp.}\ (-\varphi/kT).$$

The value of B in this equation was found to be approximately 0.1 amp./cm²/degree. The above equation is admittedly approximate. Smith[2] has derived a more exact equation which unfortunately cannot be applied in this case due to a lack of the necessary information about columbium. However, a more exact equation should not change the value of φ greatly.

Fig. 4 shows a plot of $\log_e i-\log_e T$ against $1/T$ for the positive ion currents.

During the last 100 hours of flashing treatment the positive ion currents and the work function remained constant within the limits of error, and they remained the same whether the readings were taken by changing the temperature continuously or by reducing it between readings to some lower temperature (1200°K) to keep the walls of the tube cool.

After the observations on the positive ion currents had been concluded, the electron work function was again determined and was found to be 3.97 volts. The pressure as indicated by the

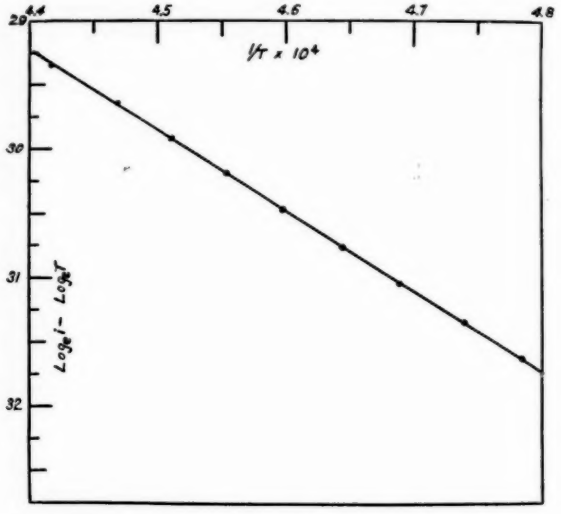

FIG. 4. Plot of $\log_e i-\log_e T$ against $1/T$ for positive ion currents.

ionization gauge was 10^{-8} mm. The average value for the electron work function from the specimens is thus 3.96 volts after correction for the Schottky effect.

The ionization gauge was now bombarded at a high temperature and again the break in the electron work function curve appeared. Heat treatment of the filament caused it to disappear as before.

Discussion of Results

The fact that the break in the electron work function curve did not appear with the second tube until after bombardment of the ionization gauge at a higher temperature than is generally used before pressure readings are taken shows conclusively that it is not characteristic of the filament. The fact that it disappears gradually and also is independent of the pressure indicates that some condensable material is volatilized from the gauge and condenses in the experimental tube. This is borne out by the fact that the break was more prominent if the bombardment was carried out with the experimental filament cold.

The vapor pressure of such a material would be determined by the temperature of the experimental tube which in turn is determined by the temperature of the filament. If the amount of the filament covered by this impurity is determined by the vapor pressure, one would expect that with continued heat treatment and as the material diffuses to the colder parts of the tube, the amount of the filament covered would be less and consequently the low temperature work function would approach the value characteristic of the pure metal.

The change in the positive ion work function is more satisfactorily explained. It is impossible to heat treat the filament for long periods at or above the temperatures at which it emits metallic positive ions since these ions generally become measurable only at temperatures where the vapor pressure becomes appreciable. If impurities which condense on the colder parts of the tube are given off during the early stages of outgassing, an equilibrium condition will be reached, with prolonged outgassing, where the vapor pressure due to these impurities will be negligible. If now the filament temperature is increased, the equilibrium will be disturbed due to the increased temperature of the colder parts of the tube and some of the impurity will volatilize. Some will also come from the comparatively cold ends of the filament. Such impurities (particularly if they are alkaline in nature) may become positively ionized on striking the hot filament and would increase the positive ion current. As the temperature of the filament is increased, this "impurity current" would increase rapidly and would tend to increase the work function. Continued flashing at the higher temperatures would establish a new equilibrium, and the effect of the impurities should disappear. Such an effect due to impurities may account for the discrepancy between Smith's and Barnes' results on molybdenum.

Magnetically Self-Focussing Streams

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Streams of fast electrons which can accumulate positive ions in sufficient quantity to have a linear density of positives about equal to the linear density of electrons, along the stream, become magnetically self-focussing when the current exceeds a value which can be calculated from the initial stream conditions. Focussing conditions obtain when breakdown occurs in cold emission. The characteristic features of breakdown are explained by the theory. Failure of high voltage tubes is also discussed.

INTRODUCTION

ALTHOUGH the focussing effect which residual gas can have on low voltage electron streams due to the fact that the ions have much smaller velocities than the electrons freed by ionization of the residual gas, has been discussed,[1] not much attention seems to have been given to the focussing effect on electron streams due to the effect of magnetic attractions between the parts of the stream. Calculation shows that such focussing can be very important at high voltages and the result explains some phenomena which occur in high voltage tubes, and which have never been satisfactorily explained. The result has a bearing on the phenomenon of breakdown in cold emission.

How such focussing can take place can be seen qualitatively by considering a stream of high velocity electrons with velocity, u, all moving parallel to a direction which we may choose as the Z-axis, and positive ions moving with velocity, v, in the opposite direction. The density of electrons, positives, and residual gas are assumed to be small and collisions infrequent. The force acting between any two electrons has components[2]

$$F_x=(1-u^2/c^2)E_x;\quad F_y=(1-u^2/c^2)E_y;\qquad F_z=E_z;\quad (1)$$

where E_x, E_y and E_z are the components of the force which would exist if the electrons were not moving, i.e., the familiar Coulomb force. The force acting between any two positives has components

$$F_x'=(1-v^2/c^2)E_x';\ F_y'=(1-v^2/c^2)E_y';\qquad F_z'=E_z';\quad (2)$$

and the force between any electron and positive

$$F_x''=(1+uv/c^2)E_x'';\ F_y''=(1+uv/c^2)E_y'';\qquad F_z''=E_z''.\quad (3)$$

If the density of positives everywhere equals the density of electrons, the static attractions and repulsions cancel, but the additional magnetic force in every case is an attraction so that the charge in every element of volume attracts the charge in every other element of volume. In a cylindrically symmetric stream which is of uniform composition along its length, and which is long compared with its diameter, the attraction between each small element of volume and any long thin element of the stream parallel to the axis, varies inversely as the radial distance from the first small element to the axis of the long thin element, and so the potential energy of the first small element is proportional to the integral of the logarithm of the radial distance to the various long thin elements of volume.

The stream could not spread out indefinitely because in so doing, the potential energy of the stream would approach a logarithmic infinity. No single electron or positive could leave the stream indefinitely far because its individual potential energy would approach a logarithmic infinity. Hence positives in such a stream could

[1] Johnson, J.O.S.A. and R.S.I. **6**, 701 (1922) and Buchta, J.O.S.A. and R.S.I. **10**, 581 (1925).

[2] See Mason and Weaver, *Electromagnetic Field*, p. 299.

not leave it except by moving out of one of the ends, unless there were more positives than electrons, in which case, only enough would leave the stream to equalize the numbers of each kind of particle per unit length of stream.

The hypothesis of positives at the same density as electrons is not so improbable of realization as might have appeared at first sight, both because the velocity of a positive is much smaller than that of an electron formed by the same collision, and also because the positives once formed in the stream have to pass down the stream clear to the end. An electron freed by the same collision that formed a positive, is acted upon by an attractive force which is much smaller than that acting on the high velocity electrons in the stream, as may be seen from the form of expressions (1). The force between the slow electron the Z-component of whose velocity is u', and each fast electron with velocity u, has components

$$F_x'''=(1-uu'/c^2)E_x'''; \quad F_y'''=(1-uu'/c^2)E_y'''; \quad F_z'''=E_z'''.$$

Since u' is much smaller than u, the attractive force which is proportional to $u\cdot u'/c^2$ is much smaller than the attractive force on a fast electron at the same position. A strong selection thus acts to allow the slow electrons so freed to leave the stream radially with whatever radial velocity they had after the collisions, rather than to allow them to expel the high velocity electrons. Especially in the case of high voltage streams in regions of low field in the direction of the stream will the stream tend to collect positives at high density. This hypothesis will be treated more in detail, later, after a much more definite and quantitative treatment has been given the problem.

Equilibrium Distribution

It will be convenient for the later discussion of actual streams to describe first a special distribution of the particles which is in dynamic equilibrium and which can be designated as the equilibrium distribution. This is to be a cylindrically symmetric stream having the Z-axis as the axis of symmetry. The stream consists of electrons with velocity, u, in the positive Z-direction, and positive ions having velocity, v, in the opposite direction. Superimposed on the relatively large velocity, u, the electrons are supposed to have a Maxwellian distribution of X- and Y-components of velocity so that to an observer moving parallel to the stream with a velocity, u, the number of electrons per unit length of stream with X-components of velocity between U and $U+dU$, and with Y-components between V and $V+dV$, is

$$\lambda_1\left(\frac{m}{2\pi kT_1}\right)\exp\left[-\frac{m}{2kT_1}(U^2+V^2)\right]dU\cdot dV$$

where λ_1 is the number of all electrons per unit length of stream, m is the mass of an electron, and T_1 is a constant which would be called the temperature if the Z-components of velocity were also being considered. It can be called the temperature of the electrons if it is kept in mind that temperature in this discussion means the two-dimensional temperature so defined. The distribution of Z-components of velocity does not make any difference in this problem because small variations in the kinetic energies due to Z-components of velocity cannot affect appreciably the radial distribution of the particles in the stream. Similarly, the positives are supposed to have a Maxwellian distribution of X- and Y-components of velocity superimposed on the velocity, v, in the negative Z-direction, so that to an observer moving with a velocity, v, the number of positives with X-components between U and $U+dU$, and Y-components between V and $V+dV$, is

$$\lambda_2\left(\frac{M}{2\pi kT_2}\right)\exp\left[-\frac{\mu}{2kT_2}(U^2+V^2)\right]dU\cdot dV$$

where λ_2 is the number of all positives per unit length of stream, M is the mass of a positive, and T_2 is the (two-dimensional) temperature of the positives.

Although collisions are assumed to be infrequent, and hence no thermodynamical equilibrium is being approached, it can be shown[3] that a system of particles moving in a field where the potential energy of a particle is $X(x, y)$, and having a distribution such that the number of particles between x and $x+dx$, y and $y+dy$,

[3] See Jeans, *Dynamical Theory of Gases*, p. 89.

z and $z+dz$ and with velocities between U and $U+dU$, V and $V+dV$, is

$$\rho_0\left(\frac{m}{2\pi kT}\right)\exp\left[-\frac{X(x,y)}{kT}\right]\exp\left[-\frac{m}{2kT}(U^2+V^2)\right]dx\cdot dy\cdot dz\cdot dU\cdot dV$$

will retain this distribution. The familiar derivation of this expression[4] shows that this kind of distribution is retained in spite of collisions and so it is obvious that such a distribution is retained when collisions are negligible.

A solution will now be obtained for a distribution of electrons and positives each of which has this kind of distribution, and this will be called the equilibrium distribution. This name need not include any ideas concerning how this distribution was arrived at, provided this distribution will be retained by the stream.

To an observer moving along with the electrons, the density of electrons is

$$\rho_{11}=\rho_{110}\cdot e^{-X_{11}(r)/kT_{11}}, \tag{4}$$

where ρ_{110} is the density of electrons at a radial distance where the potential energy of an electron is zero. Similarly, to an observer moving along with the positives, the density of positives is

$$\rho_{22}=\rho_{220}\cdot e^{-X_{22}(r)/kT_{22}}. \tag{5}$$

By applying Poisson's equation in the first instance, since

$$X_{11}=-e\cdot V_1$$

where V_1 is the electric potential in the first system of coordinates,

$$\nabla^2 V_1=-4\pi[-e\cdot\rho_{11}+e\cdot\rho_{21}],$$

where ρ_{11} is the density of electrons in the first system of coordinates, and ρ_{21} is the density of positives in the first system of coordinates. Substituting from Eq. (4),

$$\nabla^2\log\rho_{11}=4\pi e^2[\rho_{11}-\rho_{21}]/kT_{11}. \tag{6}$$

Analogously, on a second system of coordinates moving with a velocity, v, with the positives,

$$\nabla^2 V_{22}=-4\pi[-e\cdot\rho_{12}+e\cdot\rho_{22}]$$

and substituting from Eq. (5)

$$\nabla^2\log\rho_{22}=4\pi e^2[\rho_{22}-\rho_{12}]/kT_{22}, \tag{7}$$

where ρ_{22} is the density of positives in the second system of coordinates and ρ_{12} is the density of electrons in this system. Writing

$$4\pi e^2/kT_{11}=\alpha_1 \quad\text{and}\quad 4\pi e^2/kT_{22}=\alpha_2$$

the equations can be transformed to equations in the rest system of coordinates[5] by writing

$$\rho_{11}=\rho_1/\beta_1;\quad \rho_{12}=\beta_2[1+uv/c^2]\cdot\rho_1;\quad \rho_{21}=\beta_1[1+uv/c^2]\cdot\rho_2;\quad \rho_{22}=\rho_2/\beta_2,$$

where

$$\beta_1=(1-u^2/c^2)^{-\frac{1}{2}};\quad \beta_2=(1-v^2/c^2)^{-\frac{1}{2}}$$

and Eqs. (6) and (7) become

$$\nabla^2\log\rho_1=\alpha_1\beta_1[1-u^2/c^2]\cdot\rho_1-\alpha_1\beta_1[1+uv/c^2]\cdot\rho_2, \tag{8}$$

$$\nabla^2\log\rho_2=\alpha_2\beta_2[1-v^2/c^2]\cdot\rho_2-\alpha_2\beta_2[1+uv/c^2]\cdot\rho_1. \tag{9}$$

These are exactly the same equations as are arrived at, if, instead of using Poisson's equation in each of two moving systems of coordinates, we calculate the potential energy of each of the two kinds of particle in the rest system of coordinates, using expressions (1), (2) and (3) for the forces between particles given in the Introduction, *viz.*,

$$X_1=\int_R^r 2e\left[1+\frac{uv}{c^2}\right]\frac{d\lambda}{\lambda}\int_0^\lambda e\cdot\rho_2(\xi)\cdot 2\pi\xi\cdot d\xi-\int_R^r 2e\left[1-\frac{u^2}{c^2}\right]\frac{d\lambda}{\lambda}\int_0^\lambda e\cdot\rho_1(\xi)\cdot 2\pi\xi\cdot d\xi,$$

$$X_2=\int_R^r 2e\left[1+\frac{uv}{c^2}\right]\frac{d\lambda}{\lambda}\int_0^\lambda e\cdot\rho_1(\xi)\cdot 2\pi\xi\cdot d\xi-\int_R^r 2e\left[1-\frac{v^2}{c^2}\right]\frac{d\lambda}{\lambda}\int_0^\lambda e\cdot\rho_2(\xi)\cdot 2\pi\xi\cdot d\xi,$$

[4] The derivation usually includes the distribution in the Z-component of velocity, too, but since the potential function is not a function of z, the distribution in the Z-component of velocity cannot affect the density.

[5] A discussion of the relativistic transformation of density can be found in Eddington's *Mathematical Theory of Relativity*, p. 33, *et seq.*

where R is the radial distance from the axis at which the potential energy is zero. These can be substituted in the Boltzmann expressions (4) and (5) (taking logarithms and derivatives to put the equations into the form of (8) and (9)) if we keep in mind that the temperatures in the rest system must be relativistically transformed from those in the moving systems by

$$T_1=\beta_1\cdot T_{11};\quad T_2=\beta_2\cdot T_{22}$$

because the two-dimensional temperatures used here are proportional to the transverse kinetic energies in which the mass and transverse velocities must be transformed.

Since exactly the same equations are obtained regardless of which method of approach to the problem is used, even to the extent of being relativistically invariant, we are justified in using expressions (1), (2) and (3) for the forces on the particles in the later treatment of non-equilibrium cases.

A particular solution of (8) and (9) is

$$\begin{aligned}\rho_1&=\rho_0/[1+b\rho_0 r^2]^2\\ \rho_2&=\frac{\alpha_1\beta_1[1-u^2/c^2]+\alpha_2\beta_2[1+uv/c^2]}{\alpha_2\beta_2[1-v^2/c^2]+\alpha_1\beta_1[1+uv/c^2]}\cdot\rho_1,\end{aligned}\qquad(10)$$

where

$$b=\frac{\alpha_1\alpha_2\beta_1\beta_2}{8c^2}\cdot\frac{(u+v)^2}{\alpha_1\beta_1[1+uv/c^2]+\alpha_2\beta_2[1-v^2/c^2]}.$$

This solution is of course relativistically invariant.

If the ratio of the density of electrons to the density of positives in each of any two elements of volume in the stream, swept out by passing two small elements of cross-sectional area along the entire stream parallel to the axis, is greater than

$$\frac{1+v/c}{1-u/c}\quad\text{or less than}\quad\frac{1-v/c}{1+u/c}$$

it is seen from the application of expressions (1), (2) and (3) given for the forces between particles, in the Introduction, that the charge in any two such elements would repel and an equilibrium distribution with such ratios present is impossible. Thus, although expressions (10), are only a particular solution, they are a very good approximation to the complete solution for the distribution when the velocities u and v are small compared with the velocity of light, c, and in fact no serious error will be introduced by setting the coefficient in Eqs. (10) equal to unity. This makes the approximate solution

$$\rho_1=\rho_2=\rho_0/[1+b\rho_0 r^2]^2,$$

where

$$b=\frac{\pi e^2}{2kc^2}\cdot\frac{(u+v)^2}{T_1+T_2}.\qquad(11)$$

The number of either kind of particle per unit length of stream is

$$\lambda_0=[c^2\cdot 2K(T_1+T_2)]/e^2(u+v)^2\qquad(12)$$

and the current is

$$i_0=[c^2\cdot 2K(T_1+T_2)]/e(u+v),$$

which is rigidly fixed by the values of u, v, T_1 and T_2. Thus an equilibrium distribution of the kind just described can exist only for one special value of the current. This will be designated as the critical current.

Sources and Distributions of Positives

At electron velocities corresponding to potential drops of the order of 5000 volts and larger, the probability that a collision with a neutral molecule will result in ionization is to a good approximation (except when the velocities approach that of light) inversely proportional to the voltage of the primary electron.[6] The number of ions formed by each electron per centimeter of path from gases more apt to be present in tubes at moderately high vacuum, can be esti-

[6] See J. J. Thomson, *Conduction of Electricity through Gases*, Vol. 2, 3rd Ed., p. 96, *et seq.*

mated at least for order of magnitude as $200p/V$, where p is the pressure in mm of mercury, and V is the potential of the electrons in e.s.u. If the current in e.s.u. in a stream of fast electrons is i, the number of ions formed per centimeter length of stream, per second, is $200pi/Ve$. If it is supposed that these ions are formed in a region having a uniform field intensity, E, the number of ions per centimeter length of stream coming from along the stream back a distance, d, is

$$200\frac{p}{V}\cdot\frac{i}{e}\cdot\left(\frac{2Md}{Ee}\right)^{\frac{1}{2}},$$

where M is the mass of an ion. For this to be equal to or greater than the number of fast electrons per centimeter length of stream

$$\frac{i}{e}\left(\frac{m}{2Ve}\right)^{\frac{1}{2}}\leq 200\frac{p}{V}\cdot\frac{i}{e}\left(\frac{2Md}{Ee}\right)^{\frac{1}{2}}$$

and so the pressure of the gas must be, approximately

$$p\geq 2\cdot 10^{-7}(VE/Wd)^{\frac{1}{2}}, \qquad (13)$$

where V and E are in volts, and volts per centimeter, respectively, and W is the molecular weight of the gas from which the ions are formed. If the actual gas pressure exceeds the value calculated from expression (13) for the conditions at any part of the stream, the number of positives per unit length of stream will exceed the number of fast electrons at that part of the stream.

In addition to the residual gas as a source of ions, we must keep in mind that it has been found in numerous cases[7] that large amounts of the anode material can be removed from the anode by high voltage streams. This necessarily increases the density of matter in the vicinity of the stream while large electron currents are passing.

In order to see what is to be expected to be the kinetic energy of the positives after they are formed, some experiments by Ishino[8] can be considered in which it was found that when fast electrons are passed through a rarefied gas, the electrons freed in ionizations have transverse kinetic energies distributed so that about ninety percent of the electrons have energies less than forty volts and about ten percent have energies greater than this value. Since the rapidly moving ionizing electron acts on both the atomic electron and the rest of the atom during the same interval of time, the momentum given the two must be equal and opposite so at least ninety percent of the ions must have transverse energies less than $0.022/W$ electron-volts, where W is the molecular weight. If the ions are formed from residual gas at room temperature, their velocities are not greatly affected by ionization and the average kinetic energy is approximately the energy corresponding to that temperature.

If positive ions are present at densities greater than those of the high velocity electrons, only enough of the low velocity electrons freed in the formation of positives will move directly out of the stream, to leave an average charge density only slightly positive in the stream. The static focussing field which can be obtained in this way is a small field (order of magnitude of a few volts per centimeter) similar in nature to the focussing field characteristic of the low voltage streams in the presence of gas at much higher pressure, mentioned earlier.[1]

If the positive ions have velocities much smaller than the fast electrons, as they do have except in extreme proximity to the cathode, it is apparent from the form of expressions (1), (2) and (3) that the excess of positive ions over the fast electrons, together with the neutralizing space charge of slow electrons, do not appreciably affect the motions of the fast electrons magnetically and consequently have a negligible effect on the stream. Thus in any section where there are at least as many positives as fast electrons, we are concerned with the dynamics of a stream consisting of equal numbers of each kind of particle per unit length of stream.

Stability

In order to extend this treatment to streams under conditions apt to occur experimentally, a function whose value will increase as the particles spread out from the axis can be used as a criterion of how much the stream has spread:

$$F=\int_0^\infty r^2\cdot\rho\cdot 2\pi r\cdot dr.$$

[7] Hull and Burger, Phys. Rev. **31**, 1121 (1928); Snoddy, Phys. Rev. **37**, 1878 (1931); Newman, Phil. Mag. **14**, 712 (1932); Bennett, Phys. Rev. **37**, 590 (1931).

[8] Ishino, Phil. Mag. **32**, 202 (1916).

A maximum possible value for this function can be calculated subject to the restriction that the potential energy of the stream per unit length of stream shall not exceed a value, H, which is the initial potential energy plus the sum of the kinetic energies due to components of velocity transverse to the axis, of all the particles.

Although the density of positives will not in general equal the density of electrons at all radial distances from the axis, the maximum spread occurs when the two densities are everywhere equal, so that in order to find the maximum value of F, we can write the restriction as

$$\tfrac{1}{2}\cdot(2e^2(u+v)^2/c^2)\int_0^\infty \log(r/R)\cdot 2\pi r\cdot\rho(r)\cdot dr\int_0^r \rho(\xi)\cdot 2\pi\xi\cdot d\xi = H.$$

This calculation can be simplified by using as the independent variable, n, the total number of either kind of particle from the axis out to a radial distance, r, and letting the distance, r, be dependent on n. Then

$$F=\int_0^N r^2\cdot dn \quad\text{and}\quad H=g\int_0^N n\cdot\log(r/R)dn,$$

where $g=e^2(u+v)^2/c^2$ and N is the total number of either kind of particle per unit length of stream. In order to find the maximum spread, set $\delta\{F+\lambda H\}=0$, where λ is an arbitrary multiplier. This gives a distribution with uniform density ρ' from the axis out to a radial distance, r_0, and zero beyond, where

$$\pi r_0^2\rho'=N;\quad \pi r^2\rho'=n;\quad r=r_0(n/N)^{\frac{1}{2}}.$$

If the stream is initially distributed uniformly inside a radial distance from the axis, s_0, and has a total kinetic energy due to transverse components of velocity, K, which can be related to another constant, T, by $K=2N\cdot kT$, the maximum spread is a uniform distribution out to a radial distance, r_0, given by

$$g\int_0^N n\left(\log\frac{r_0}{R}\cdot\left(\frac{n}{N}\right)^{\frac{1}{2}}\right)\cdot dn = g\int_0^N n\left(\log\frac{s_0}{R}\left(\frac{n}{N}\right)^{\frac{1}{2}}\right)\cdot dn + 2N\cdot kT,$$

i.e.,

$$r_0=s_0\cdot\exp\left[\frac{c^2\cdot 2\cdot 2kT}{e^2(u+v)^2}\cdot\frac{1}{N}\right]. \qquad (14)$$

More than half of the particles must always lie nearer the axis than $1/2^{\frac{1}{2}}$ times this value of r_0.

If the kinetic energy of the particles due to transverse components of velocity could be redistributed among the particles so that the transverse components of velocity would have Maxwellian distributions, the (two-dimensional) temperature would be T given by $K=2N\cdot kT$ and the linear density λ_0 of the stream which could have an equilibrium distribution such as given by Eqs. (12), can be substituted in expression (14). Thus more than half the particles in the stream must always lie nearer the axis than a radial distance given by

$$(s_0/2^{\frac{1}{2}})\cdot e^{\lambda_0/N}=(s_0/2^{\frac{1}{2}})\cdot e^{i_0/I}, \qquad (15)$$

where i_0 is the critical current (expression (12)) and I is the actual current.

If half of the particles get outside this radial distance, all of the transverse velocities would be simultaneously reduced to zero which is obviously impossible. Thus this expression is an exaggerated outside limit of the radial distance inside which at least half of the particles must always remain. In fact, calculation of the directions in which most of the particles would begin to drift for several special distributions show that the ratio i_0/I distinguishes between streams which begin to contract towards the axis, and those which begin to expand, the contraction occurring when $I>i_0$.

From the form of expression (15), it is seen that if the actual current is one-tenth the critical current, the radial distance inside which at least half the particles must always remain, is

liable to increase to more than 10,000 times the initial value for the outer radius of the stream, which for most experimental cases means no observable focussing action. In this sense, it may be said that the critical current given by expression (12) rather sharply distinguishes between streams which focus and those which do not. This critical current may be written as

$$i_0 = 2.5 \cdot 10^{-3} T / V^{\frac{1}{2}}, \qquad (16)$$

where i_0 is in amperes, V is the potential through which the fast electrons have fallen, in volts (except in extreme proximity to the cathode), and T is in equivalent degrees absolute, and is a constant proportional to the total transverse energy of the stream per unit length.

Applications

In an earlier communication,[9] evidence was presented supporting the contention that breakdown in cold emission is caused by positive ions liberated at the anode by small currents, and travelling back along the electron stream to the cathode. A difficulty with this idea is that even if positives do bombard the cathode in this way, still at such low densities they might be expected to eliminate any emitting areas where they strike, instead of producing them. Now this is just what has been observed to occur except when the current rises to above the order of 10^{-2} amperes. It was not clear then why this order of magnitude of the current should be so critical in changing from elimination of emitting areas to severe rupture of the cathode surface.

Focussing the positives on a small area of the cathode cannot be produced in the analogous way to the focussing of low voltage electron streams in gases at relatively higher pressures[1] by interchanging the rôles of positives and electrons, because the electrons are not produced by the positives from the residual gas as would be required by that kind of explanation.

On the other hand, if the current is momentarily large enough to give magnetic self-focussing over any considerable part of the stream, the electrons towards the anode are brought nearer the axis by this focussing action, and then since the initial total energy of positives in any part of the stream depends on the position with respect to the axis at which they were formed, and since bringing electrons nearer the axis in parts of the stream towards the anode reacts to decrease the total transverse energy of the stream per unit length in the central part where self-focussing conditions obtain, the effect of the magnetic self-focussing is to bring all particles nearer the axis over an increasingly long segment of the stream. In an analogous way, bringing the positives nearer the axis of the stream very near the cathode increases the emission from the part of the cathode delivering electrons along the axis, and this serves to decrease the total transverse energy per unit length in the central part of the stream.

This kind of process can go on indefinitely provided only that conditions for magnetic self-focussing obtain over any segment of the stream long compared with its diameter. This kind of focussing results in concentrating the positive ion current at the cathode until the current density of the positive ions is a far higher order of magnitude than the value which is known to eliminate emitting areas instead of producing them. At these higher positive ion current densities, the positives would certainly be expected to dig out the small craters which it is well known are produced during breakdown. In this way, we have an explanation of why the order of magnitude of current given by expression (16) distinguishes between breakdown and no breakdown.

It seems probable that the entire process just described takes place in a very small interval of time (order of 10^{-4} or 10^{-5} seconds) after which the streams are no longer self-focussing, because the transverse energies of the electrons arising at the ragged edges of the crater are too great, or that the density of matter near the cathode rises to so high a value that collisions can no longer be neglected with respect to the dynamics of the stream. The point of the discussion has been to show that structural defects in the cathode surface are not necessary for breakdown, but that rather, we must look to stream conditions to explain the many characteristic features of breakdown.

Any explanation of breakdown in cold emission to agree with experimental fact, should explain

[9] Bennett, Phys. Rev. **40**, 416 (1932).

the following general observations: (1) breakdown is much more abrupt when the electrodes are unoutgassed than when they are outgassed,[10] i.e., the rise of current to the maximum value permitted by the resistance in series with the source of potential is from an initially much lower value in the former than in the latter case; (2) the fineness of the polish on the surface of the cathode does not affect the value of the field intensity at which breakdown occurs[11] but only affects the fields at which the first small currents pass; (3) with unoutgassed electrodes, after breakdown has occurred, if a field intensity a little less than the field at which breakdown occurred is applied to the cathode, large sudden surges of current pass through the tube, similar in every observable respect to the surge of current which accompanied the original breakdown, but the frequency of occurrence of these surges decreases with time; (4) breakdown can be prevented, or at least its severity greatly diminished either by outgassing the electrodes (both are necessary) or by increasing the resistance in series with the source of potential[12] to a value which will limit the maximum value to which the current can rise, to the order of 10^{-3} or 10^{-4} or less; (5) before breakdown, the current is very erratic, rising abruptly, and dropping sometimes abruptly, and sometimes gradually; these erratic fluctuations while the current is small occur at values of field much higher than the values of the field for the same order of magnitude of current after breakdown; but once the value of the current has increased to more than the order of 10^{-2} amperes, the resistance of the tube decreases and the surface of the cathode becomes permanently altered to give much higher order currents at a given field than before; (6) when breakdown occurs, small flashes of light are observed both at the anode and at the cathode.

[10] Millikan and Shackelford, Phys. Rev. **15**, 239 (1920); Eyring, Mackeown and Millikan, Phys. Rev. **31**, 900 (1928); Bennett, Phys. Rev. **37**, 582 (1931).

[11] Only superficial significance was given this fact on p. 584 of the paper in Phys. Rev. **37**, 582 (1931).

[12] Unpublished work. See R. W. Mebs, Phys. Rev. **43**, 1058 (1933).

The explanation which writers have usually used in the past, *viz.*, that a particle of impurity or a piece of the metal of the cathode is torn bodily out of the cathode by the field, fails to explain the above observations, but their explanation in terms of the idea of magnetically self-focussing streams follows easily from the discussion of streams already given.

The theory of streams also explains the fact that even after electrodes have been fatigued or "conditioned" and are giving steady field-current characteristics, if the residual gas pressure is allowed to rise to the order of magnitude corresponding to expression (13) the current becomes unsteady, and the surges of current which pass can be prevented from entirely disfiguring the cathode only by increasing the resistance in series with the source of potential.

The fact that the field intensity for breakdown in mercury obtained recently by Beams[13] agrees so well with the results of the writer for other metals with a similar arrangement of electrodes shows that surface impurities can at most only serve to give the first small electron currents, but that an entirely different explanation is necessary in order to explain breakdown.

The theory of streams explains the fact that the experience with tubes to which extremely high potentials are applied[14] has been that destructive cold emission occurs at fields of the order of 100,000 volts per centimeter, but that the application of fields of the order of 1,000,000 volts per centimeter to surfaces prepared in the same way, but held at much shorter distances from the anode were found by the writer to be necessary to produce measurable emission. In the case of high voltage tubes, the longer distances and the higher voltages both aid in the formation of self-focussing streams.

In conclusion, the writer wishes to thank Professor L. H. Thomas of this laboratory, for the very generous assistance which he has given in discussions of mathematical methods.

[13] J. W. Beams, Phys. Rev. **44**, 803 (1933); Bennett, Phys. Rev. **37**, 582 (1931).

[14] Lauritsen and R. D. Bennett, Phys. Rev. **32**, 850 (1928); Breit, Tuve and Dahl, Phys. Rev. **35**, 51 (1930); Lauritsen and Cassen, Phys. Rev. **36**, 988 (1930); Lauritsen, Phys. Rev. **36**, 1680 (1930).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Surface Ionization of Potassium on Tungsten

According to a recent communication by Copley and Phipps,[1] the efficiency of ionization of potassium by hot tungsten is considerably greater than corresponds to the modified Saha equation, when the constants in it are given their usually accepted values. This equation is

$$\frac{\nu_+}{\nu_a}=\frac{1-r_+}{1-r_a}\cdot\frac{\omega_+}{\omega_a}\exp\left[\frac{(\phi-I)\epsilon}{kT}\right],$$

where ν_+/ν_a is the ratio of the rates of evaporation of ions and atoms, r_+ and r_a are the reflection coefficients, ω_+ and ω_a the statistical weights, $\epsilon\phi$ the work function of the tungsten, and I the ionization potential of potassium. The value of $(1-r_+)/(1-r_a)$ is usually assumed to be 1, ω_+/ω_a is $\frac{1}{2}$, and I is 4.32 volts. The work function of tungsten was taken by Copley and Phipps to be 4.52 e.v. With these values of the constants they obtained theoretical values of ν_+/ν_a only about half as great as those found experimentally.

It was pointed out by Copley and Phipps that it would be possible to reconcile their results with the requirements of the theory by assuming $(1-r_+)/(1-r_a)$ to have a value of about 2, instead of 1, so that it would cancel out the weight factor ω_+/ω_a. There is, however, an alternative way in which an apparently too high ν_+/ν_a could be accounted for, namely, by assuming for ϕ *in the operating range of temperatures* values substantially higher than that corresponding to the slope of a Richardson line for tungsten. As the writer has pointed out elsewhere,[2] the decrease in the concentration of free internal electrons associated with thermal expansion must tend to make ϕ increase with temperature, and it may easily be shown that the order of the rate of increase due to this cause is the same as would account for the measured value of the constant A, assuming the transmission of electrons through the emitting surface to be practically perfect.

The experimental range covered by Copley and Phipps extends, in round figures, from 1600° to 2500°K. Let us see what values of ν_+/ν_a might be expected at both these extreme temperatures and also at some intermediate temperature, say 2000°K. The electron emissions obtained from well-aged tungsten at 1600°, 2000° and 2500°K per *apparent* cm² of surface are 9.27×10^{-7}, 1.00×10^{-3} and 2.98×10^{-1} amp., respectively. According to Tonks,[3] the "roughness factor" for tungsten etched by heat treatment must be *at least* 1.225. We shall probably not be far wrong if we take a round 1.3 for this quantity. This would make the emissions per true cm² at the three temperatures 7.13×10^{-7}, 7.69×10^{-4} and 2.29×10^{-1} amp., respectively. From these data it is a simple matter to calculate the corresponding values of ϕ on the assumption that the true A has the theoretical value for perfect transmission, namely, 120 amp. cm^{-2} degree^{-2}. The values obtained in this way are 4.65, 4.68 and 4.72 volts, respectively. If these are now substituted in the modified Saha equation, $(1-r_+)/(1-r_a)$ being assumed equal to 1, values for ν_+/ν_a equal to 5.48, 4.06 and 3.20, respectively, are obtained. The corresponding ionization efficiencies are 84.6, 80.2 and 76.2 percent, respectively. These are represented by the crosses in Fig. 1. It will be seen that they agree with the experimental results, which are represented by the circles, within what appear to be the limits of experimental uncertainty.

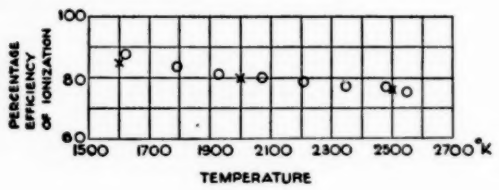

FIG. 1.

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General Electric Company, Ltd.,
Wembley, England,
May 10, 1934.

[1] M. J. Copley and T. E. Phipps, Phys. Rev. **45**, 344 (1934).
[2] Letter to be published shortly in Nature.
[3] L. Tonks, Phys. Rev. **38**, 1031 (1931).

New Band System in Nitrogen—an Addition and Correction

Soon after writing a paper for this journal under the above title I received a letter from Professor G. Herzberg of Darmstadt in which he gave another formula for the bands, and consequently a new interpretation for the initial electronic state. The formula given by Herzberg is

$$\nu=49774.4+(1446.46v'-13.93v'^2)-(2345.16v''-14.445v''^2)$$

and the initial state is therefore the metastable $A\,{}^3\Sigma$ state.

I argued against this interpretation in my paper, but a little consideration showed me that the initial electronic level is the $A\ ^3\Sigma$ level. I hesitated to make the major correction on the proof that this change would require, and it is for that reason that I present the alternative arguments here. Furthermore, it will be of interest to compare the arguments given here with that presented in my paper.

If we use Herzberg's formula and extrapolate the vibrational levels of the upper state by the method of Birge and Sponer we obtain a value of 10.4 volts for the total energy. If we use my formula, the value is 9.3 volts. In either case the values obtained by extrapolation are too high if our experience with this method is a good criterion. If we assume that the initial level is the $A\ ^3\Sigma$ level, then Sponer's value of 8.18 volts for this level must be lowered to 6.14 volts and, as I pointed out in a paper in this journal,[1] the heat of dissociation of 9.4 volts which was obtained in that paper has to be lowered by the same amount, thus making the heat of dissociation 7.4 volts. Since $A\ ^3\Sigma$ dissociates into a ^4S and a ^4D atom, its total energy should be 9.8 volts. This is less than the calculated value of 10.4 volts, but that is what one would expect. If we assume that $D(N_2)$ is 7.9 volts then the total energy should be 10.3 volts, and this agrees entirely too well with the 10.4 volt value obtained by extrapolation.

If we assume that the initial level is a new triplet level which dissociates into two ^4S atoms, then its total vibrational energy should be either 1.2 or 1.7 volts depending on the choice of 7.4 or 7.9 volts for $D(N_2)$. The extrapolation yields 3.1 volts for this energy, and it is seen that this is more than twice as large as 1.2 and about 80 percent larger than the 1.8 volt value. In either case, the error seems to be unusually large even for the extrapolation method. It seems therefore that the initial level is the $A\ ^3\Sigma$ level.

Another argument leads to the same conclusion. This new band system in gaseous N_2 corresponds to the ϵ-system observed by Vegard in the luminescence of solid N_2.[2] In this system many more bands have been observed than in the gaseous system, and it was possible to calculate the average separations between the vibrational levels of the upper state. Nine pairs of bands originating on $v'=5$ and 6 gave an average difference of 1293 cm^{-1} for these two vibrational levels. The average of the observed differences as taken from the first-positive band system for which the $A\ ^3\Sigma$ level is the lower level is 1292 cm^{-1}. The difference obtained from the formula given in my paper is 1229 cm^{-1}. A similar argument for the difference between $v'=4$ and 5 gives an average of 1323 cm^{-1} from 11 pairs of bands of the ϵ-system, and an average of 1323 cm^{-1} for this difference from the observed first-positive bands, and a calculated value of 1271 cm^{-1} from my formula. It must be concluded therefore that the initial level is the $A\ ^3\Sigma$ level and that the heat of dissociation of nitrogen is 7.4 volts. A discussion of the connection between this new value and the electron impact measurements of Lozier and of Tate, Smith and Vaughan has been given in a letter in these columns by Dr. Lozier.

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University of California, at Los Angeles,
May 18, 1934.

[1] Kaplan, Phys. Rev. **42**, 100 (1932).
[2] Vegard, Zeits. f. Physik **75**, 44 (1932).

The Absorption Spectrum of Diatomic Arsenic

A new system of some eighty absorption bands has been discovered in the spectrum of arsenic between 2200A, and 2750A, which can be definitely assigned to the diatomic molecule. This includes the five faint fluorescence bands observed by Rosen[1] and tentatively ascribed to As_2. The whole system bears a striking resemblance to that of P_2, investigated by Herzberg,[2] where $\Delta G''$ is about 750 cm^{-1} and $\Delta G'$ 470 cm^{-1}. A preliminary analysis gives for arsenic ΔG values that are about 420 cm^{-1} for the lower and 270 cm^{-1} for the upper state. The vibrational levels of both states converge very slowly.

The emission spectrum of phosphorus is attributed by Herzberg to a $^1\Sigma_g^+ \leftarrow\!\!- {}^1\Sigma_u^+$ transition, in which the upper potential curve is crossed by another, possessing a flat minimum and a lower heat of dissociation, which is either a $^3\Sigma_u^+$ or a $^3\Pi_u$ state. This causes predissociation in the upper and perturbation of the lower vibrational levels of the $^1\Sigma_u^+$ state. The plot of the $\Delta G'$ values of our arsenic bands shows a discontinuity at $v'=4$, which appears to represent perturbation similar to that observed by Herzberg.

G. E. GIBSON
A. MACFARLANE[3]

Department of Chemistry,
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Berkeley, California,
May 18, 1934.

[1] Rosen, Zeits. f. Physik **43**, 69 (1927).
[2] Herzberg, Nature **126**, 239 (1930); Ann. d. Physik (5), **15**, 677 (1932).
[3] Commonwealth Fellow.

Note on the Thermal History of the Earth

In a previous paper[1] the problem of the cooling of the earth has been treated under the simplifying assumption that the surface of the earth is either permanently at 0° or that it radiates into a medium at 0°.

The object of the present note is to amplify the treatment of the previous paper by taking into account the heat received from the sun.

If λ designates the average value of the solar constant, defined as the amount of heat received from the sun at the surface of the earth per unit area per unit time during normal incidence, then the total average rate of heat from

[1] Lowan, *On the Cooling of a Radioactive Sphere*, Phys. Rev. **44**, 769 (1933). This paper will be referred to as A.N.L.

the sun is $Q=\pi R^2\lambda$. For the sake of simplicity, it may be assumed that the earth is subjected to a uniform flux of heat of magnitude $Q/4\pi R^2=\lambda/4$.

The function $T(r, t)$ must then satisfy the Eqs. (1), (2) and (3) of A.N.L., and the new boundary condition

$$\partial T/\partial r+\sigma T=\lambda/4K=q \quad \text{(say)} \tag{4'}$$

when $K=$coefficient of thermal conductivity and $\sigma=$coefficient of heat transfer, and it is assumed that the surrounding medium is at 0°.

If we make the substitution

$$T(r, t)=q/\sigma+v(r, t) \tag{A}$$

it is readily seen that the function $v(r, t)$ must satisfy the Eqs. (1) and (3) of A.N.L. while (2) and (4') become

$$\lim_{t\to 0} v(r, t)=f(r)-q/\sigma, \tag{2'}$$

$$\partial v/\partial r+\sigma v=0 \qquad r=R. \tag{4''}$$

The system (1), (2'), (3) and (4''), is analogous with the system considered in A.N.L., and the solution of which is given by (21). If, for the sake of brevity, this solution is designated by $\theta(r, t)$, the complete solution of the more general problem here considered is

$$T(r, t)=\frac{q}{\sigma}\left\{1-\frac{2}{r}\sum_{n=1}^{\infty} e^{-k\lambda_n^2 t} \times\frac{(h^2+\lambda_n^2)\sin\lambda_n r}{R\lambda_n^2+h(Rh+1)}\int_0^R \xi\sin\lambda_n\xi d\xi\right\}+\theta(r, t),$$

where the summation extends over the roots of the transcendental equation

$$\lambda\cos\lambda R+h\sin\lambda R=0 \tag{B}$$

and where $h=\sigma-1/R$.

With the aid of (B) we get

$$\int_0^R \xi\sin\lambda_n\xi d\xi=-(1/\lambda_n)(R+1/h)\cos\lambda_n R.$$

Our solution thus finally becomes

$$T(r, t)=\frac{q}{\sigma}\left\{1+\frac{2(Rh+1)}{rh}\sum_{n=1}^{\infty}\frac{(h^2+\lambda_n^2)\cos\lambda_n R\sin\lambda_n r}{\lambda_n\{R\lambda_n^2+h(Rh+1)\}} \times e^{-k\lambda_n^2 t}\right\}+\theta(r, t).$$

The expression in brackets is the correction term due to the heat received from the sun.

ARNOLD N. LOWAN

Institute for Advanced Study,
Princeton, New Jersey,
May 21, 1934.

The Azimuthal Effect of Cosmic Rays

It seems of interest to note in view of the recent studies of cosmic rays, principally by T. H. Johnson,[1] A. H. Compton,[2] and A. H. Compton and R. J. Stephenson,[3] that certain unusual observed features of the rays follow immediately from rather simple theoretical considerations.

It has been noted[4] that the observed state of rest of ionized calcium clouds in interstellar space guarantees that all such regions are field free and electrically neutral to a high degree of approximation.

The observed neutral state can be demonstrated to be entirely stable in the following manner. Consider a closed region immersed in an electrically conducting space and suppose that the free charge inside the closed region is Q. Then employing Gauss' theorem and noting that the current density across the boundary is the product of the conductivity σ and the electric field E we have

$$-dQ/dt=\sigma\int\int E\cdot dS=4\pi\sigma Q \quad \text{whence} \quad Q=Q_0\epsilon^{-4\pi\sigma t}$$

and therefore the magnitude of the free charge will be reduced to $1/\epsilon$ its value in a time $\tau=1/4\pi\sigma$. Now the density of radiation in interstellar space is appreciable and of course the pressure is very low so that a large fraction of all interstellar atoms are ionized. (For example, the interstellar calcium clouds are made up of ionized atoms.) It is therefore proper to employ the conductivity of an ionized gas in calculating the relaxation time τ. The conductivity an ionized gas is readily shown to be independent of pressure and is given by

$$\sigma=9\overline{kT}^{\frac{3}{2}}/8\pi 6^{\frac{1}{2}}e^2m^{\frac{1}{2}},$$

where m is the mass of the conducting ion, e its charge and kT its thermal energy. Thus, upon substitution of numerical values, it is found that $\tau\leq 10^{-8}$ sec., where we have taken the worst possible conditions, i.e., assumed that the conducting ion is a heavy calcium ion and taken T at an improbably low value of 3°K.

Thus, since a free electric charge in interstellar space will be neutralized in 10^{-8} sec., we conclude that all interstellar space is electrically neutral and therefore cosmic rays cannot be generated in such regions.

It is further clear that ions, all of one sign, cannot traverse interstellar space and it is necessary that each ion have associated with it a neutralizing mate. Thus we have been led to insist that cosmic rays are essentially *ion pairs*.[4]

Consider a typical stream of ions in space. If the positive ions (say) should move faster than the neutralizing negative ions it is clear that a separation of charge would result and the region would not be neutral. Further the electric field set up by the assumed separation of charge would retard

[1] Johnson, Phys. Rev. **43**, 834 (1932); **44**, 856 (1933); **45**, 569 (1934).
[2] A. H. Compton, Phys. Rev. **43**, 387 (1933).
[3] A. H. Compton and Stephenson, Phys. Rev. **45**, 441 (1934).
[4] R. Gunn, Terr. Mag. and Atm. Elec. **38**, 247 (1933).

the positive ions and accelerate the negative ions until they synchronized in velocity. We may therefore assert that the observed *neutrality of space requires that equal numbers of positive and negative ions must traverse space with identical velocities.*

We think that this necessary state of affairs accounts for the observed predominance of positive cosmic-ray ions in the lower atmosphere, because if the velocities of any two ions are equal, both the kinetic energy and momentum are proportional to their respective rest masses. Thus if a primary cosmic ray is composed of a proton or calcium ion and an electron, then since the ratio of each velocity to that of light is the same, the ions will describe spiral paths in the earth's magnetic field with effective radii proportional to their rest masses. Thus ion pairs entering the earth's magnetic field will be torn apart (unless they happen to be separated by nearly atomic distances[4]) and the electron will be bent toward the west at great altitudes and describe spirals of relatively small radius, but the positive component of the primary pair will have momentum at least 1840 times that of the electron and it will be bent toward the east describing a spiral of correspondingly great effective radius. It is noteworthy, too, that the energy of the incoming positive ion is also very great compared to that of the associated electron and it will penetrate to greater depths. On both counts, therefore, the predominance of positive ions is to be expected at the earth's surface and, of course, the positive ions will have a maximum intensity from the west.

Rough calculations lead to satisfactory agreement with the observed azimuthal distribution if it is assumed that the incoming ion pairs are predominantly protons, or heavier ions neutralized in each case by an electron. (A positron-electron pair is definitely excluded because their masses are presumably identical.)

The separation of charge resulting from the selective action of the earth's magnetic field on the ion pairs produces a terrestrial electric field in the high atmosphere which seems unimportant for cosmic rays but provides a mechanism for producing the auroral discharge if cosmic-ray-like ion pairs of lower energy are discharged from the sun in sufficient numbers. It has been shown that although the sun could not emit cosmic rays, it might produce great numbers of ion pairs of 10^5 e.v. energy[4] and the above selective action appears adequate to describe the aurora in detail.

The present conclusions are independent of any theory of the origin of cosmic rays and follow directly from their ionic nature and the observed neutrality of interstellar space. However, the author's theory of their origin which indicates that they are emitted from certain types of "blue" stars is consistent with the conditions here imposed and is in agreement with many addditional data.[4]

Ross Gunn

Naval Research Laboratory,
Washington, D. C.,
May 31, 1934.

Radioactivity Induced by Neutron Bombardment

The experiments of Fermi[1] and Dunning (unpublished results on the induced β-particle emission from elements bombarded by neutrons) give added information concerning the nature of the nucleus. It leads to the idea that the ensemble of protons and neutrons forming the nucleus exert an appreciable force on the negative energy electrons within the nucleus and are thus capable of producing pairs —positron and electron. Whether this process occurs will depend on the value of the transition probability from the state in which the ψ-function represents the initial ensemble of protons and neutrons to that state in which the ψ-function represents the final ensemble of protons and neutrons together with a pair, positron and electron.

Thus if we have a reaction in which the neutron is captured by the element X_ρ^m and remains in that nucleus in an excited state, then through the possibility of the formation of a pair the following reaction can take place: the combination of the neutron with the positron to form a nuclear proton with the subsequent emission of the electron provided a transition is possible from the element $(X+n)_\rho^{m+1}$ to the element $(X+n)_{\rho+1}^{m+1}$. The possibility of this latter transition will depend on the value of the transition probability from the ψ-function representing the state $(X+n)_\rho^{m+1}$ to the ψ-function representing the final state $(X+n)_{\rho+1}^{m+1}$ together with a free electron. The idea that the selection rules governing the transition probability are a determining feature in nuclear reactions has been developed previously by Fermi,[2] and Bramley.[3]

Only further experiments can decide whether the nuclear pairs are produced by the nuclear protons or whether the neutrons have the power themselves to produce pairs.

These selection rules must be such that there cannot be more protons in the nucleus than neutrons, e.g., the series, $H^1D^2T^3He^4$. These rules indicate that T^3 should have a very small chance of forming a pair with the subsequent formation of He^3 and the emission of a free electron whereas T^3 should react readily with neutrons to form He^4 with the emission of a free electron. Whether the excess energy will appear as energy of the free electron or as hard γ-rays it is impossible to state.

We shall take as our final example, the case of the neutron bombardment of carbon. The reaction $C_6^{13}+n_0^1 \rightarrow C_6^{14} \rightarrow N_7^{14}+\epsilon^-$ is possible on this model but a radioactive reaction following the formation of $C_6^{13}C_6^{12}+n_0^1 \rightarrow C_6^{13}$ is improbable as C_6^{13} cannot make a transition to another existing element with the emission of an electron.

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[1] Fermi, Nature **133**, 757 (1934).
[2] Fermi, Zeits. f. Physik **88**, 161 (1934).
[3] Bramley, Science **79**, 160 (1934).
[4] Kemble and Present, Phys. Rev. **44**, 1031 (1933).

The process by which the nuclear electron, formed as one entity of the pair, escapes from the nucleus, is difficult to imagine. It may be that the nuclear barrier for electrons is much lower than we have supposed: the calculations of Kemble and Present[4] on the fine structure of Hα indicate an effective nuclear radius of 5×10^{-12} cm; the calculations of the writer[5] on the formation of x-rays by high energy electrons lead to a similar conclusion; the reaction $D^2+D^2 \rightarrow T^3+H^1$ requires an even larger effective collision radius to explain the rate of reaction.

ARTHUR BRAMLEY

Bartol Research Foundation
of the Franklin Institute,
May 31, 1934

[5] Bramley, Nature **133**, 259 (1934).

Artificial Radioactivity Using Carbon Targets

It has been reported[1] and apparently substantiated[2, 3] that when carbon is bombarded with protons a radioactive element is produced which has a decay-period exactly the same as that of the radioactive element produced when carbon is bombarded with deutons. As reported at the Washington Meeting of the American Physical Society, however, preliminary observations in this Laboratory showed that any effect produced by protons bombarding carbon was certainly less than one percent of that produced by deutons. A more refined measurement has now been made which shows conclusively that in the experiments in other laboratories the effect could have been produced only by deutons present as a contamination in the "proton"-beam. The reaction originally reported, therefore, does not occur and the problem of accounting for an identical decay-period for the two cases does not exist.

The experiment was performed as follows. An ionization-chamber 8 cm in diameter and 5 cm long was connected to an FP-54 amplifier, operated at a sensitivity of 1×10^{-16} ampere per millimeter, and arranged for photographic registration. A thin (0.01 mm) aluminum window was provided at the top of the chamber so that electrons and positrons could enter. Carbon disks (Acheson Graphite, 1 cm diameter and 1 to 2 mm thick) were first bombarded with either protons or deutons in the high-voltage tube and then removed and placed with the bombarded face against the ionization-chamber window.

The results obtained when such a target was bombarded with deutons (total mass-two spot not more than 0.5 microampere at about 1000 kv) is given in Fig. 1. The effect was great enough so that the measuring instrument could be run at one-one hundredth sensitivity, giving the smooth curve shown. After the first 6 minutes, the curve was accurately exponential, giving a half-life of 10.4 minutes for the radioactive element produced. Although this agreement in the decay-period with those given by the previous workers might be taken as support for the radionitrogen hypothesis, we are not yet satisfied as to the identity of the elements involved or the reaction (reactions?) occurring.

The corresponding result obtained when a similar disk was bombarded with protons (mass one spot, two microamperes) is shown in Fig. 2. This trace was taken at full

[1] Cockcroft, Gilbert and Walton, Nature **133**, 328 (1934).
[2] Crane and Lauritsen, Phys. Rev. **45**, 497–498 (1934).
[3] Anderson and Neddermeyer, Phys. Rev. **45**, 653 (1934).

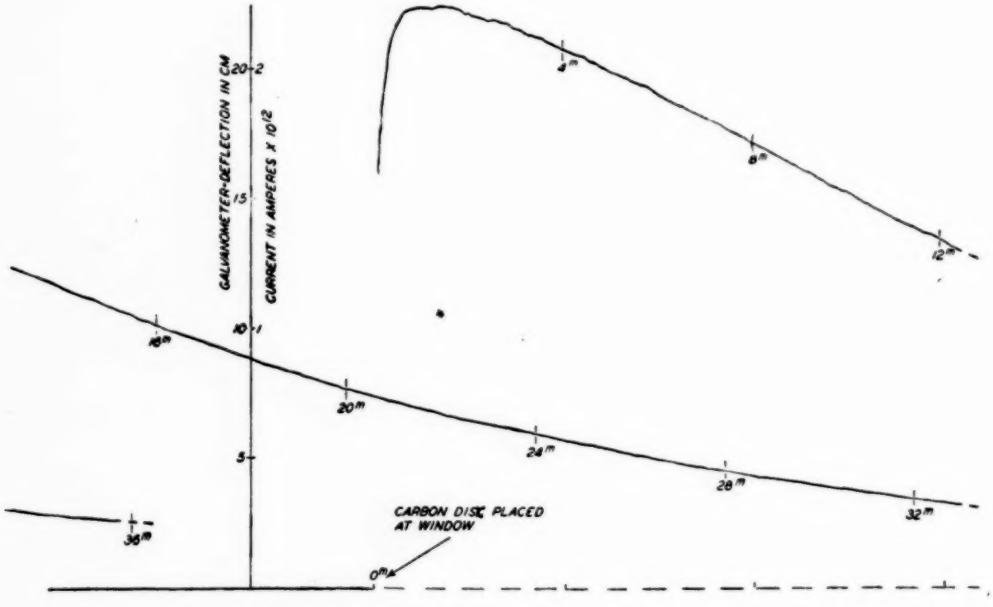

FIG. 1. Radioactivity from deutons on carbon.

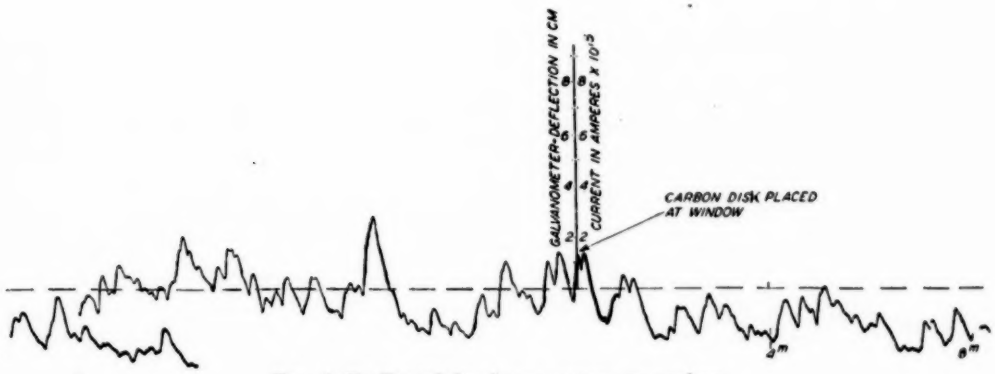

FIG. 2. Radioactivity from protons on carbon.

sensitivity and, in spite of the raggedness of the trace at this extreme sensitivity, a displacement of the mean of about one centimeter could have been detected. This would be one-two thousandth of the effect measured in Fig. 1 and, since the proton-current used was four times the deuton-current, we may conclude that any effect produced by protons on carbon is less than one-eight thousandth of the effect produced by deutons. [Incidentally, this is additional evidence for the extreme purity of our proton-beam after magnetic analysis, as previously reported.]

The wide discrepancy between this result and those reported by the workers in Cambridge and Pasadena does not appear to us to be particularly surprising, since magnetic analysis evidently was not used in their experiments. While it is true that in the experiments at Pasadena residual contamination by deuterium would hardly be expected to amount to 10 percent or 20 percent of the total beam, it is quite possible that the total beam with deuterium flowing might contain only five to ten times as many deutons as with the deuterium-flow cut off. In some of our previous work we determined the yields of several efficient disintegration-processes by working for many days with no deuterium-flow, that is, using only the residue of deuterium left in the tube from previous runs. Further evidence that the percentage of deutons in the Pasadena experiments is much lower than estimated is given by the higher gamm-ray yields from carbon and beryllium we have observed.[4]

We take great pleasure in expressing our gratitude to Professors Urey, Zanetti, and La Mer, of Columbia University, for the supply of deuterium which made these experiments possible.

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Department of Terrestrial Magnetism,
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Washington, D. C.,
June 1, 1934.

[4] Hafstad, Tuve and Brown, Phys. Rev. **45**, 746–747 (1934).

On the Limitations of the Theory of the Positron

In a recent paper[1] Dirac has suggested a further development of his theory of the positron. Dirac here considers the operators corresponding to charge and current density for a system of electrons in which nearly all the negative energy states are full, and shows that in the presence of an arbitrary external electromagnetic field these operators may be divided into two terms: one of these is infinite, and depends on the field but not on the state of the electrons; the other is finite and determinate, and depends on the field and on the electron state. Dirac makes the suggestion that these second terms be regarded as giving the charge and current density of the electron-positron distribution (*epd*): i.e., that the formalism of his theory of the electron be modified by the subtraction from the operators for charge and current density of the infinite and field-dependent terms. This modification leaves unaltered the Lorentz and gauge invariance of the theory and the validity of the conservation law for charge and current. Because, however, the way in which the operators are to be modified depends upon the value of the electromagnetic field, the method is not readily extended to take account of the field produced by the *epd*; on the other hand, it gives for the charge and current induced in the *epd* by an external field finite and definite results, and thus constitutes in this respect a true theoretical advance.

In the further development of Dirac's suggestions one meets, however, with a curious difficulty, in that it is apparently impossible to find a consistent definition of the operators for the energy and momentum density of the *epd*. Dirac's density matrix, of course, makes possible a complete formal definition of any operator, which one obtains, in analogy with the methods of the quantum mechanics, by taking the matrix product of the matrix corresponding to the variable in question and the density matrix. This is just what Dirac has done for the current density. If one carries this through for the energy momentum tensor of the *epd*, one finds in general that its divergence is not given by the Lorentz force with Dirac's expressions for the charge and current. This is because the electromagnetic

[1] P. Dirac, Proc. Camb. Phil. Soc. **30**, 150 (1934).

potentials enter explicitly in the density matrix, and lead to the existence of non-Maxwellian forces. With this definition of the dynamical operators, one has thus to abandon either Dirac's expression for the charge and current density or the validity of the conservation laws for energy and momentum. In particular one would not otherwise obtain consistent results, in computing on the one hand the induced charge density, and on the other the polarization energy, of the *epd* in an electrostatic field.

The simplest way of obviating these difficulties is to modify the density matrix in a way which does *not* depend on the electromagnetic field strengths present: i.e., to subtract from the operator given by the Dirac theory of the electron the expressions for the state of the electron distribution in the absence of external fields, for which all negative states are full. This procedure leads directly to the theory of the positron as we have developed it. On this theory one finds a polarization of a vacuum by an electromagnetic field which is infinite, and which can only be rendered reasonably unambiguous by special conventions about the way in which the divergent expressions occurring are to be handled.[2] This theory is therefore not only unable in general to predict the reaction of the *epd* to its own field, but can make no unambiguous statements about the fields induced by the *epd* under the influence of a given external field.

Nevertheless we believe that these difficulties in no way impair the limited validity of the theory of the positron, a validity which is limited to those questions which do not involve essentially the reaction of the electrons and positrons to their own radiation fields and thus does not extend to problems in which there are external fields whose frequency is of the order of the critical value mc^3/e^2. For at least insofar as the fields are themselves produced by electrons and positrons, the polarization of the *epd* manifests itself[3] in effects which are not unambiguously separable from the unknown effects of the radiation reaction of the particles. An instructive illustration of this may be found in the question of the fluctuations of the charge density of the *epd*, which was brought to our attention by Dr. Bloch. If we consider, for instance, the case of an empty *epd* in no external field, for which the expectation value of the charge density vanishes everywhere, we readily find that the expectation value of the square of the charge within any volume is infinite, corresponding to the fact that there are infinite fluctuations in the charge density. If we now ask in what measure it is possible to observe these fluctuations, we see that, to detect them, we must have an observing system (e.g., galvanometer) which will react in accordance with the electron-theoretic laws to electromagnetic fields of arbitrarily high frequency. If we admit that our instruments will not respond to waves of frequency large compared to mc^3/e^2, then we see at once that the *observed* fluctuations in the charge density will be finite and small, and that the paradoxical predictions of the theory of the positron are quite without physical consequences.

There exists the possibility, which is suggested by classical electron-theory, that we should have in the proton a particle which would respond in accordance with Maxwellian electrodynamic to waves of frequency far greater than mc^3/e^2, and that by its use the effects of the polarization of the *epd* could be separated from the problems of radiation reaction. There is, however, a growing mass of experimental evidence that so simple a theory of the proton can hardly be correct, and which lends support to the view that the present electrodynamics will be inapplicable in all questions involving lengths of the order of e^2/mc^2. From this point of view the paradoxes of the theory of the positron would be inextricably connected with those of quantum electrodynamics, and the applicability of the two theories would be similarly limited.

It must of course be remarked that the condition that in the field acting upon the charges there be no components of frequency of the order of mc^3/e^2 or greater is a sufficient, but by no means a necessary condition for the applicability of present electrodynamics, for this condition is clearly not relativistically invariant. The necessary condition, as Bohr particularly has emphasized, is that there exist a coordinate system in which such high frequency components are absent, insofar at least as one may consequently neglect the reaction of the charges to their own field. On the other hand, it is not in general possible to infer that, if in a given Lorentz frame high frequency components appear, the reaction of the charges to the low frequency components is correctly given by the Lorentz force. It is for this reason that one need not regard as altogether cogent the arguments recently advanced by v. Weizsaecker[4] for the validity of the theoretical formulae for the behavior of very high energy radiations in their passage through matter, formulae which are in fact very difficult indeed to reconcile with experiment.

W. H. FURRY*
J. R. OPPENHEIMER

Pasadena,
June 2, 1934.

[2] Thus Peierls, to whom we are indebted for telling us of his results, has developed a method by which the polarization of the *epd* in an arbitrary electromagnetic may be computed in first order in a gauge and Lorentz invariant manner.

[3] W. H. Furry and J. R. Oppenheimer, Phys. Rev. **45**, 245 (1934); pages 261–2.

[4] L. F. v. Weizsaecker, Zeits f. Physik **88**, 612 (1934).

* National Research Fellow.

A New Mode of Disintegration Induced by Neutrons

The capture of a neutron followed by the ejection of an α-particle is now a well-known process in the disintegration of light nuclei. Thus in nitrogen this may be written:

$$_7N^{14}+{}_0n^1={}_5B^{11}+{}_2He^4.$$

Using as a source of neutrons beryllium bombarded by 3 MV deutons, which were accelerated in the Lawrence-Livingston[1] apparatus, I have photographed six examples of a disintegration in which the emitted particle is of smaller charge than an α-particle and is probably a proton. The judgment is based on the character of the trace left

[1] E. O. Lawrence and M. S. Livingston, Phys. Rev. **45**, 608 (1934).

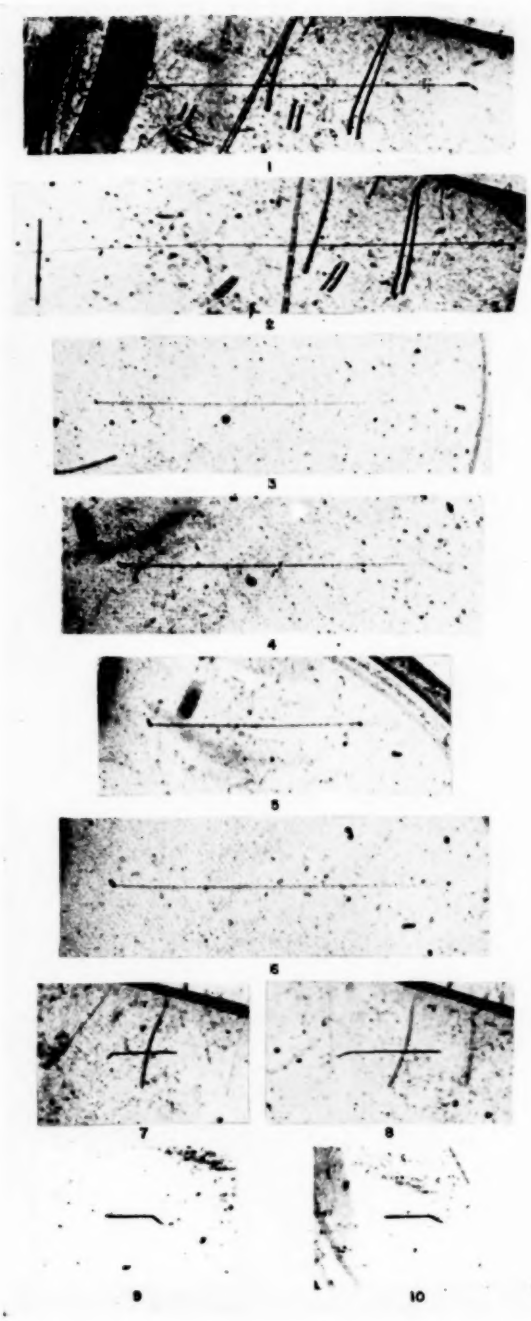

FIG. 1. Pairs of photographs of disintegration forks. Magnification about 0.6. 1, 2; 3, 4; 5, 6 are forks of the new type in which a proton is emitted instead of the usual α-particle. In 1, 2 the proton, proceeding from right to left hits the glass side wall of the chamber and in 3, 4 and 5, 6 the proton, proceeding from left to right, hits the floor of the chamber before reaching the end of its range. 7, 8; 9, 10 are pairs of photographs of the usual mode of disintegration. Attention is directed to the great difference in density of the short and long tracks in the first six pictures as compared to the last four.

in a Wilson cloud chamber by the disintegration, consisting of a short heavy track joined to a long thin track. The latter may equally well be a proton, a deuton or a nucleus of the newly discovered isotope of hydrogen ${}_1H^3$; but, since protons are known to exist in light nuclei and to emerge as such in many types of disintegration, we shall assume these particles to be protons.

To unravel the numerical relations in a disintegration fork one needs at least three facts; any three of the following will do: the lengths of the two tines, the angle between them and the direction of motion of the incident neutron. It is greatly to be desired that all four be known, for the fourth fact can be used as a check on the reaction chosen to represent the transmutation. Here we know only the length of the tine attributed to the nucleus and the angle between the two tines. Scattering in the iron which forms part of the apparatus used to accelerate the deutons introduces chaos in the directions from which the neutrons arrive at the cloud chamber. The evidence to distinguish these forks from the usual ones must be got from an examination of their photographs. Several of these are shown in Fig. 1 along with some of the ordinary type for comparison.

The cloud chamber contained both nitrogen and oxygen when the forks were photographed so that it is not possible to decide what reaction took place. Any of the following six may represent the fork:

$$\begin{aligned} {}_7N^{14}+{}_0n^1 &= {}_6C^{14}+{}_1H^1, \\ &= {}_6C^{13}+{}_1H^2, \\ &= {}_6C^{12}+{}_1H^3; \\ {}_8O^{16}+{}_0n^1 &= {}_7N^{16}+{}_1H^1, \\ &= {}_7N^{15}+{}_1H^2, \\ &= {}_7N^{14}+{}_1H^3. \end{aligned}$$

The second and third possibility in each case have the abundance of the new nucleus in their favor. The first possibility involves the creation of ${}_6C^{14}$ or ${}_7N^{16}$ neither of which corresponds to a known isotope of these elements. However, Fermi[2] has been led to postulate reactions of this type (emission of a proton) to explain the chemical processes necessary to entrain the β-ray activity induced in many elements by neutrons, so that it seems likely that ${}_6C^{14}$ or ${}_7N^{16}$ may emit an α-particle and return to the element originally struck by the neutron. Whether or not N or O is made radioactive by neutrons has not been conclusively established. If they are we shall have exchanged a neutron for a proton and an electron with presumably no permanent alteration in the nucleus originally struck by the neutron.

It is a pleasure to acknowledge the generous assistance given to me by Professor E. O. Lawrence in placing laboratory facilities at my disposal, in discussions and in practical aid in these experiments.

FRANZ N. D. KURIE*

Radiation Laboratory,
Department of Physics,
University of California,
May 31, 1934.

[2] E. Fermi, La Ricerca Scientifica, Anno V, Vol. I, March, April, 1934.

* National Research Fellow.

Proceedings of the Metropolitan Section of the American Physical Society

MEETING OF MARCH 24, 1934

THE first regular meeting of the Metropolitan Section was held in Room 401, Physics Laboratories, Columbia University, New York, New York on Saturday, March 24, 1934. Morning and afternoon sessions were held. The presiding officer was Professor G. B. Pegram, Chairman of the Section except during part of the afternoon when Dr. W. S. Gorton, Vice-Chairman, presided.

About 200 were present at each of the sessions. Both sessions were devoted to invited papers except for two short intervals devoted to the election of officers for the next year. The following were elected:

Chairman	G. BREIT
Vice-Chairman	H. C. UREY
Secretary-Treasurer	W. S. GORTON
Elected Members of the Executive Committee	S. L. QUIMBY
	G. P. HARNWELL

Those who presented papers at the invitation of the Section, and their subjects, were as follows:

Sloan's Resonance Method of Producing High Voltages, F. M. EXNER, *Crocker Institute for Cancer Research.*

The Acceleration of Ions by Moving Electrical Fields, J. W. BEAMS, *University of Virginia.*

Discussion of Professor Beams' Method, W. S. GORTON, *Bell Telephone Laboratories.*

Production and Measurement of Penetrating X-Rays, F. K. RICHTMYER, *Cornell University.*

Experiences and Research with a 700 kv *K*-Ray Installation, G. FAILLA, *Memorial Hospital.*

The Technique of Focussed Ion-Beams Using Cascade Tubes and Electrostatic Generators, M. A. TUVE, *Department of Terrestrial Magnetism, Carnegie Institution of Washington.*

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